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Mercury Photosensitized Reaction of Cyclo-octatetraene and the Comparison with the Direct Photochemical Reaction

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(Received December 28, 1957)

Both experimental and theoretical investigations on cyclo-octatetraene have been made in our laboratory[1-6]. Among them the experiment of the direct photochemical reaction[3,6], the spectroscopic studies[1,4] and the calculation of energy levels[2] relate closely to the present work.

Cyclo-octatetraene has two singlet excited states near 2800 Å and 2000 Å[1,4], through which the direct photochemical reaction takes place[3,6]. According to the calculation of the molecular orbitals, however, several triplet states are expected to exist in the vicinity of these singlet states[2,7]. In view of the spin correlation rule, cyclo-octatetraene may react via the triplet states in the mercury photosensitized reaction[8]. In order to distinguish between these two processes, the mercury photosensitized reaction has been compared experimentally with the direct photochemical reaction, because even in the latter the reaction mechanism has not yet been clarified in the preceding works[3,6]. The experiment was carried out in vapor phase in the presence or the absence of mercury vapor, using mercury resonance line, λ2537, under both flow and static conditions, and the preliminary study on the decomposition reactions has already been reported[9]. In the present study, to elucidate the whole reaction mechanism, decomposition, isomerization and polymerization processes have been investigated quantitatively.

Experimental

Static Method. — The apparatus ordinarily used is shown in Fig. 1. The light source is a quartz mercury resonance lamp wound in the form of a spiral. The lamp was operated from the secondary of a transformer which maintained a current of 100 mA through the lamp and provided a starting potential of 1000 V. In its operation the potential drop across the lamp was 500 V. The lamp emits a small amount of radiation at 1849 Å, which is absorbed by oxygen in the light-path of 15 cm. in length. The light from the lamp was collimated by a quartz lens, in order to make the light nearly parallel at the reaction cell. The absolute light intensity was measured by a uranyl actinometer[10], which was placed behind the reaction cell. The light intensity at 2537 Å was approximately 3.7×10^{16} photons/sec.

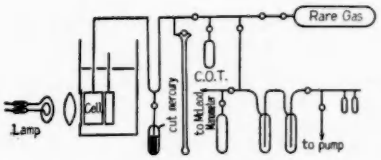

Fig. 1. Apparatus of static system.

Before starting an experiment, the fused-quartz reaction cell (4 cm. long and 5 cm. in diameter) was removed from the system, cleaned with hot chromic acid solution and flamed out. Adding small droplets of distilled mercury, the reaction cell was then attached to the system using de Khotinski cement on the standard taper joint. The de Khotinski cement was chosen because cyclo-octatetraene is insoluble in it. The reaction cell was immersed in a distilled water bath, thermostated at 20.0°C. A definite amount of cyclo-octatetraene vapor was then introduced into the cell and isolated by a mercury cut which served also as a manometer.

At the end of an experiment, the lamp was turned off and the condensable products in the reaction cell were frozen in a trap with liquid nitrogen. The noncondensable gas at dry ice temperature was transferred into a trap with liquid nitrogen through another trap with dry-ice in methanol. After the distillation was completed, the pressure in this part of the system was measured by a small McLeod gauge. The gas mixtures which were noncondensable at dry-ice temperature were analyzed by a mass spectrometer. A Beckman spectrophotometer model

1) I. Tanaka and S. Shida, This Bulletin, **23**, 54 (1950).
2) Y. Mori, I. Tanaka and S. Shida, ibid., **23**, 168 (1950).
3) I. Tanaka, S. Miyakawa and S. Shida, ibid., **24**, 119 (1951).
4) S. Miyakawa, I. Tanaka and T. Uemura, ibid., **24**, 136 (1951).
5) S. Shida and S. Fujii, ibid., **24**, 173 (1951).
6) I. Tanaka and M. Okuda, *J. Chem. Phys.*, **23**, 1780 (1955).
7) P. Schiess and Mme. A. Pulman, *J. chim. phys.*, **53**, 101 (1956).
8) K. J. Laidler "The Chemical Kinetics of Excited States", Clarendon Press, Oxford (1955), p. 32.
9) H. Yamazaki and S. Shida, *J. Chem. Phys.*, **24**, 78 (1956).
10) J. N. Pitts et al., *J. Am. Chem. Soc.*, **77**, 5499 (1955).

D. U. and Hilger E2 type spectrograph were used for the analysis of the products which were condensable at dry-ice temperature.

In the case of the direct photochemical reaction, the absence of mercury vapor has to be fully checked, since the same reaction system is used for those two kind of experiment. The detection of mercury vapor was made by the mercury photosensitized reduction of tungsten oxide in the presence of hydrogen. The greenish tungsten oxide powder turned black for a few minutes of irradiation in the presence of a small amount of mercury vapor. In its absence, however, there was no appreciable change in color even after two hours' irradiation.

In the case of the direct photochemical reaction, oil manometers were used in place of mercury manometers. The small amount of mercury vapor, when left in the system, was trapped with liquid nitrogen. In addition, gold and indium foils, placed in the side tube of the reaction vessel, were used for the removal.

For avoiding the mercury photosensitization, another supplementary experiment was made using the reversed resonance line. The light source was a hot mercury lamp operated by 100 V. D. C. The broadened resonance line was then filtered by a quartz cell containing mercury vapor and hydrogen as quencher.

Flow Method.—The light source was a low-pressure mercury-rare-gas lamp of U-type, which was operated at nearly the same power supply as that for the spiral-type lamp in the static method described before. The dimension of the reaction tube was 20 cm. long and 2.5 cm. in diameter.

In a typical experiment, cyclo-octatetraene was introduced into the reaction system at a linear flow rate, which was controlled by the two cocks placed at both ends of the reaction cell. The cyclo-octatetraene pressure in the reaction tube was measured by a mercury or an oil manometer. During an experiment the product was condensed into the trap immersed in liquid nitrogen. The lamp current was adjusted to a fixed value. At the end of the irradiation, the lamp and the cyclo-octatetraene stream were shut off and the condensable gas in the system was frozen in the trap. The analysis of the products is similar to that in the static method.

Effect of the Addition of Rare Gases.—Since these reactions are supposed to proceed through the excited state of cyclo-octatetraene, the investigation on the deactivation of excited cyclo-octatetraene is of interest. Rare gases are chosen as the quenchers, because of their negligibly small quenching cross section towards the excited mercury atom relative to that of cyclo-octatetraene, and the result is compared with that of ethylene.

The experiment was made in the static system. A definite amount of cyclo-octatetraene was introduced into the reaction cell and condensed with dry-ice. Then a definite amount of the rare gas was added. The system was allowed to stand for four hours for mixing before irradiation. After the reaction was completed the rare gas was gradually pumped off through a trap with liquid nitrogen, in which the acetylene produced was trapped. The amount of acetylene was determined by a method already described. The rare gases which were spectroscopically pure were commercially obtained, and cyclo-octatetraene furnished by the Mitsubishi Kasei Co., was purified by repeating the recrystalization and vacuum distillation.

Result

Decomposition Reaction. — Both in the mercury photosensitized reaction and the direct photochemical reaction, no gas noncondensable at the liquid nitrogen temperature, such as hydrogen and methane, was detected, and the noncondensable at the dry-ice temperature was acetylene. Since acetylene and benzene were produced in the same amount in the mercury photosensitized reaction as well as in the direct photochemical reaction, their appearance seems to be the result of the molecular decomposition. The rate and the quantum yield of the decomposition reaction as a function of cyclo-octatetraene pressure were shown in Fig. 2 and Fig. 3 respectively, in which the rate of the decomposition reaction is that measured by the acetylene produced. In the case of mercury photosensitized reaction, quantum yield of decomposition as a function of cyclo-octatetraene pressure has a maximum; it may be considered that below this pressure the quantum yield decreases on account of the incomplete

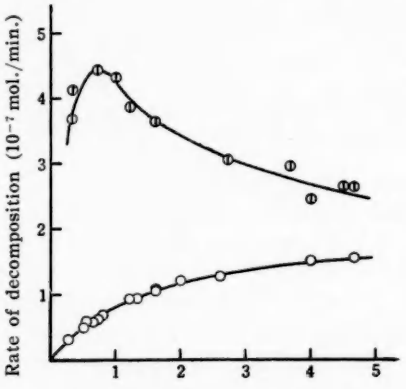

Fig. 2. Rate of decomposition as a function of C.O.T. pressure.
◑: Mercury photosensitized reaction
○: Direct photochemical reaction

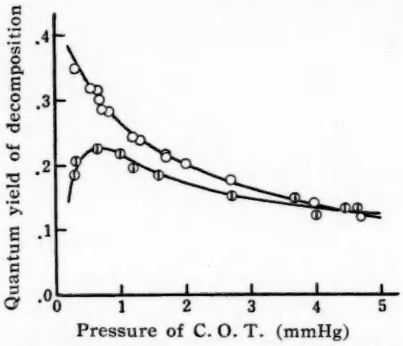

Fig. 3. Quantum yield of decomposition as a function of C. O. T. pressure.
◑: Mercury photosensitized reaction
○: Direct photochemical reatcion

quenching of the excited mercury atom by cyclo-octatetraene molecule and, above this pressure, the quantum yield also decreases on account of the collisional deactivation of the excited cyclo-octatetraene molecule by the normal cyclo-octatetraene. Such a type of behavior has previously been observed with ethylene. In the case of the direct photochemical reaction, however, the quantum yield of decomposition decreases monotonically as increasing cyclo-octatetraene pressure by the collisional deactivation. Plotting the reciprocal of the quantum yield, ϕ_d, of the decomposition reaction against the pressure of cyclo-octatetraene, straight lines were obtained, which are shown in Fig. 4. From the intercept of the ordinate by these lines, the limiting quantum yield of decomposition can be estimated as 0.3 and 0.4 for the mercury photosensitized reaction and the direct photochemical reaction, respectively.

In the experiment with the reversed light source, the rate of the decomposition reaction as a function of pressure of cyclo-octatetraene is shown in Fig. 5. This is similar to the result in the direct photochemical reaction in absence of mercury vapor.

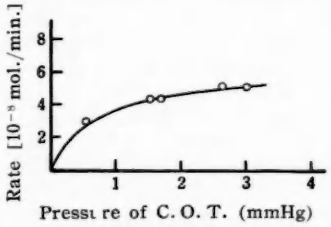

Fig. 5. Rate of decomposition as a function of C. O. T. pressure.
(A filter containing mercury vapor and hydrogen gas was used.)

Polymerization and Isomerization Reaction.—As the reaction proceeds, a thin yellowish film deposits in front of the reaction cell, which seems to owe to the polymerization of cycro-octatetraene. To examine the polymerization reaction, the total pressure change and the amount of acetylene produced were measured in the course of reaction in the complete quenching region of cyclo-octatetraene pressure for the excited mercury atom. The result of the experiment was shown in Fig.

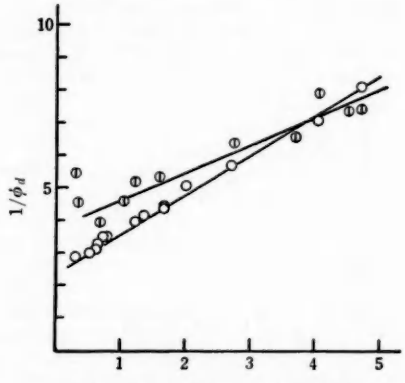

Fig. 4. Plots of $1/\phi_d$ as a function of C. O. T. pressure.
◑: Mercury photosensitized reaction
○: Direct photochemical reaction

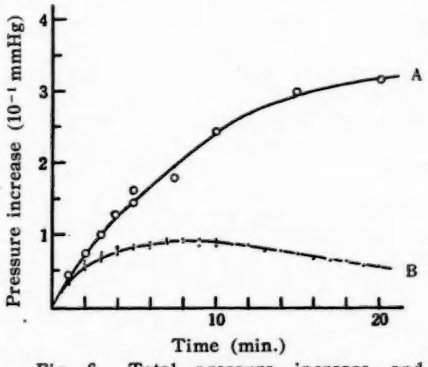

Fig. 6. Total pressure increase and acetylene production in the course of reaction.
A: Acetylene production
B: Total pressure change

6, in which the total pressure initially increased, reaching a maximum after about seven minutes' irradiation and then began to decrease slowly; the production of acetylene on the other hand increased monotonically except that the rate of production gradually decreased on account of the filtering effect by the polymeric clinging to the front of the reaction cell. In this experiment the amount of acetylene produced was measured after the reaction was complete in each run. By removing acetylene produced, no change was observed in the behavior of the total pressure variation in the course of the reaction. Therefore it may be considered that acetylene does not act as an intermediate of the polymerization reaction and furthermore the secondary effect of acetylene is ignored in this reaction. After irradiation, absorption spectra of the mixture of reaction products and cyclo-octatetraene were measured in methanol solu ion. The result was shown in Fig. 7, in which there

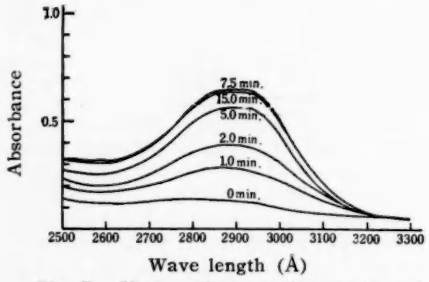

Fig. 7. Change of absorption spectrum in the course of reaction.

is seen a marked increase in absorption spectra at the wave length near 2900 Å. The product shows orange color due to the fact that the foot of this absorption is in a visible region. This absorption spectrum shows also the band structure at 3050, 3005, 2912 and 2820 Å in the gas phase spectrogram. The absorption spectra gradually increased and reached a maximum value after about seven minutes' irradiation as observed for the total pressure change in Fig. 6.

The spectra of unirradiated cyclo-octatetraene, that obtained after 20 minutes' irradiation and that preserved for a week in vacuo are shown together in Fig. 8. The orange colored liquid, which seems to be an isomer of cyclo-octatetraene, is unstable and during the presservation in vacuo for a week, a yellowish plastic substance was obtained which is

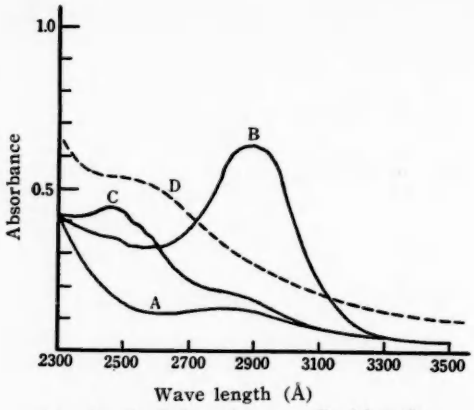

Fig. 8. A: Before the run. B: After the run. C: After the run and a week stored in vacuo. D: Polymer film dipositted in front of the reaction cell.

partially soluble in hexane and shows an absorption near 2600 Å. In this polymerizing process there is no evidence that noncondensable gases in dry-ice temperature such as acetylene and hydrogen are produced. The orange colored liquid may be polymerized without decomposition.

In an attempt to examine the initial stage of the reaction just described more precisely, a series of runs was made under the flow condition. The relative amount of the orange-colored liquid produced was measured by the absorption at 5000 Å using the pure cyclo-octatetraene as the reference. An experiment has been made on the pressure dependence of the production of orange-colored liquid in comparison with that of acetylene production, only in the mercury photosensitized reaction. The result, as shown in

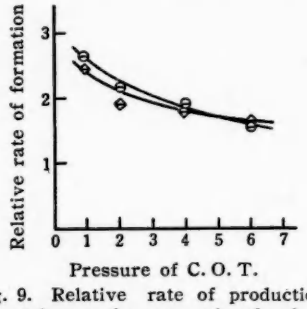

Fig. 9. Relative rate of production of acetylene and orange-colored substance in mercury photosensitized reaction. ⊖ Acetylene ◇ Orange-colored substance (Different scales were used for two kinds of products).

Fig. 9, almost coincides with that of acetylene production.

The relative amount of acetylene and orange-colored liquid has been investigated both in the mercury photosensitized reaction and the direct photochemical reaction. The plots against the time of the relative amount of these products were shown in Fig. 10. The ratio of the production of orange-colored liquid to that of acetylene

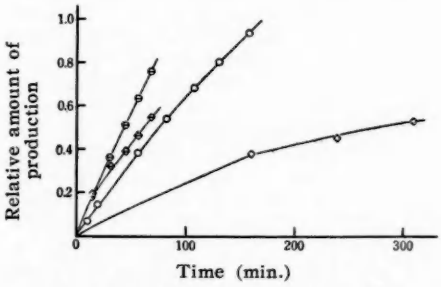

Fig. 10. Relative amounts of production of acetylene and orange-colored substance. ⊖ Acetylene ⊜ Orange-colored substance (mercury photosensitized reaction); ○ Acetylene ◇ Orange-colored substance (direct photochemical reaction) (different scales were used for two kinds of products).

is twice as great in the photosensitized reaction as in the direct photochemical reaction. Assuming the extinction coefficient of the orange-colored liquid at 2900 Å as 10^4, the ratio of orange-colored liquid to acetylene is about 2:1 and 1:1 in the mercury photosensitized reaction and the direct photochemical reaction, respectively. In the forgoing experiment, as the limiting quantum yield of decomposition was 0.3 and 0.4 for the mercury photosensitized reaction and the direct photochemical reaction, respectively, it may be considered that the whole excited cyclo-octatetraene molecules would undergo either the decomposition reaction or the isomerization giving orange-colored liquid in the limiting case in which the pressure of cyclo-octatetraene is zero.

Styrene Formation.—In the case of the mercury photosensitized reaction, for over 20 minutes' irradiation, new absorption spectral lines at 2800 Å and 2880 Å appeared in the gas phase spectrogram of the reaction products, which coincide with that of styrene. The amount of styrene produced was about one-tenth of benzene and therefore we performed no further quantitative experiment on this product, because this seems to make little contribution to the elucidation of the reaction mechanism.

Effect of the Addition of Rare Gases.—As shown in Fig. 2 and Fig. 9, the rate of the decomposition reaction and that of the formation of orange-colored liquid decrease with increase in the pressure of cyclo-octatetraene. Then it may be considered that the excited cyclo-octatetraene molecule is deactivated by cyclo-octatetraene itself. The collisional deactivation of excited cyclo-octatetraene was also investigated, measuring the change in the quantum yield of the decomposition reaction by mixing rare gases.

The reciprocal of the quantum yield of decomposition measured by the amount of acetylene produced is plotted against the pressure of rare gases in Fig. 11, in which there is seen a fairly well linear relationship between these two quantities.

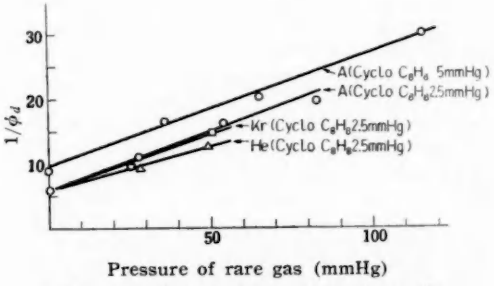

Fig. 11. Plot of the reciprocal of the quantum yield of decomposition as a function of rare gas pressure.

Discussion

In an attempt to explain the experimental result, the reaction will be discussed in terms of a sequence of reactions which is somewhat similar to the one proposed for ethylene; however, in addition the discussion includes the reactions producing orange-colored liquid (presumably bicyclo form of C_8H_8) and polymer. The reaction mechanism is as follows:

$$Hg + h\nu \rightarrow Hg^* \quad (a)$$

$$Hg^* \rightarrow Hg + h\nu \quad (b)$$

$$C_8H_8 + Hg^* \rightarrow C_8H_8^*(\text{triplet}) + Hg \quad (1)$$

$$C_8H_8^*(\text{triplet}) + C_8H_8 \rightarrow 2C_8H_8 \quad (2)$$

$$C_8H_8^*(\text{triplet}) \rightarrow C_2H_2 + C_6H_6 \quad (3)$$

$$C_8H_8^*(\text{triplet}) \rightarrow \text{bicyclo } C_8H_8 \quad (4)$$

$$\text{bicyclo } C_8H_8 + Hg^* \rightarrow \text{bicyclo } C_8H_8^* + Hg \quad (5)$$

$$\text{bicyclo } C_8H_8^* + \text{wall} \rightarrow \text{polymer} \quad (6)$$

For the direct photochemical reaction in place of step 1 the following two processes may be considered,

$$C_8H_8 + h\nu \rightarrow C_8H_8^*(\text{singlet}) \quad (1a)$$

$$C_8H_8^*(\text{singlet}) \rightarrow C_8H_8^*(\text{triplet}) \quad (1b)$$

Even in the case of mercury photosensitized reaction, it will be possible for the direct light absorption by cyclo-octatetraene molecules to occur. The absorption coefficient of mercury vapor at room temperature for mercury resonance line is about 3 $cm.^{-1}$ [11], while the absorption coefficient for several mmHg of cyclo-octatetraene is 0.1 $cm.^{-1}$, the extinction coefficient of the latter at 2537 Å being 300 l./mol. cm.[1,4] Hence the mercury resonance line was selectively absorbed by mercury vapor under the condition studied; the reaction 1a will be ignored in comparison with reaction 1.

Making use of the usual stationaly state assumption, we find the concentration of of Hg^* and $C_8H_8^*$ to be

$$[C_8H_8^*] = k_1[C_8H_8][Hg^*]/(k_2[C_8H_8] + k_3 + k_4) \quad (1)$$

$$[Hg^*] = I_{abs}/(k_b + k_1[C_8H_8]) \quad (2)$$

The rate of acetylene production is given by

$$d[C_2H_2]/dt = k_3[C_8H_8^*] \quad (3)$$

Eqs. 1 and 2 are introduced into Eq. 3 to give the quantum yield of decomposition, ϕ_d, as a function of cyclo-octatetraene,

$$\phi_d = k_1k_3[C_8H_8]/(k_1[C_8H_8] + k_b)(k_2[C_8H_8] + k_3 + k_5) \quad (4)$$

Similarly in the case of the direct photochemical reaction we have

$$\phi_d' = k_3'/(k_2'[C_8H_8] + k_3' + k_4') \quad (5)$$

The pressure dependence of the quantum yield of the decomposition can be interpreted by the formulae 4 and 5 in the pressure range studied; thus in the mercury photosensitized reaction the quantum yield of decomposition has a maximum, while in the case of the direct photochemical reaction the quantum yield of decomposition monotonically decreases as cyclo-octatetraene pressure increases.

The reaction rate constants in the sequence of reactions can be estimated from the formulae mentioned above: k_b, the reciprocal of the life time of the excited mercury atom, $Hg(6^3P_1)$, is 10^7 $sec.^{-1}$ [12], and from the slope of the straight line in Fig. 4 the value of k_2/k_3 is 2.1×10^7 cc./mol., and as we have described (Result, polymerization and isomerization reaction) k_3/k_4, the ratio of formation of acetylene to the orange-colored liquid, is 0.5. If the excited cyclo-octatetraene molecule is deactivated by one collision with the normal cyclo-octatetraene molecule, then assuming the collisional diameter as 6 Å, the life time of the excited cyclo-octatetraene molecule is calculated to be 10^{-8} sec.

Similarly in the case of the direct photochemical reaction the ratio of the reaction constants can be estimated from Fig. 4 as $k_2'/k_3' = 2.5\times10^7$ cc./mol. and $k_3'/k_4' = 1$, which is the same order of magnitude as those of the mercury photosensitized reaction.

Differentiating Eq. 4 with respect to $[C_8H_8]$ and putting it to be zero, then the following expression is obtained:

$$k_1 = (k_3 + k_4)k_b/k_2P_0^2 \quad (6)$$

where P_0 is the pressure of cyclo-octatetraene corresponding to the maximum ϕ_d.

Introducing the reaction rate constants estimated before into Eq. 6, k_1 becomes 10^{15} cc./sec. mol., from which the quenching cross section of the excited mercury atom by cyclo-octatetraene is to be 10^2 Å^2, which is of reasonable magnitude.

The collisional deactivation of the excited cyclo-octatetraene molecule may be explained by the following reaction in addition to the above sequence,

$$C_8H_8^*(\text{triplet}) + M \rightarrow C_8H_8 + M \quad (7)$$

where M is rare gas.

The quantum yield of decomposition is then represented by the following equation,

$$\phi_d = k_1k_3[C_8H_8]/(k_1[C_8H_8] + k_b) \times (k_2[C_8H_8] + k_7[M] + k_3 + k_4) \quad (7)$$

which can be reduced, under the condition for the complete quenching of the excited mercury atom, to

$$\phi_d^{-1} = k_7[M]/k_3 + \text{const.} \quad (8)$$

The relative efficiencies of deactivation calculated from the slope of the lines in Fig. 11 are 0.13, 0.19 and 0.17 for helium, argon and krypton respectively, taking the efficiency of cyclo-octatetraene as unity.

The deactivation cross section calculated

11) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms", Cambridge Univ. Press, Cambridge (1934) p. 203.

12) see reference 11) p. 147.

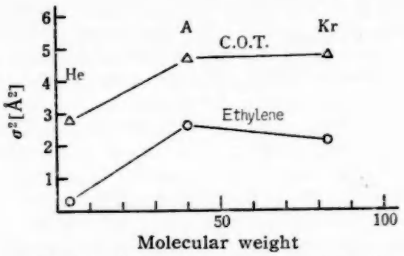

Fig. 12. Quenching cross section of excited C. O. T. and ethylene molecule by rare gases.

from these values were shown in Fig. 12 together with those of ethylene[13], where the cross section for self-deactivation were taken as 30 Å^2 and 11 Å^2 for cyclo-octatetraene and ethylene respectively by considering the geometrical dimension. There is seen a parallel dependence of the cross section on the molecular weight of the deactivating gases.

The estimation of the rate constants can also be made on the isomerization and the polymerization path,

$$\begin{aligned} &\mathrm{d}[\text{bicyclo } C_8H_8]/dt \\ &\quad = k_4[C_8H_8^*] - k_5[\text{bicyclo } C_8H_8][Hg^*] \\ &\quad = k_1k_4[C_8H_8][Hg^*]/(k_2[C_8H_8] + k_3 + k_4) \\ &\qquad - k_5[\text{bicyclo } C_8H_8][Hg^*] \end{aligned} \quad (9)$$

Integrating Eq. 9 [bicyclo C_8H_8] is given as a function of time:

$$[\text{bicyclo } C_8H_8] = A\{1-\exp(-Bt)\} \quad (10)$$

where the constants A and B are given by

$$A = k_1k_4[C_8H_8]/k_5(k_2[C_8H_8] + k_3 + k_4) \quad (11)$$

and

$$B = k_5I_{abs}/(k_1[C_8H_8] + k_b) \quad (12)$$

For the formation of the polymer, the following equation will be obtained,

$$\mathrm{d}[P]/dt = k_5[\text{bicyclo } C_8H_8][Hg^*] \quad (13)$$

Integrating the equation, the amount of polymer produced is given by

$$[P] = ABt + A\{\exp(-Bt) - 1\} \quad (14)$$

The experimental result shown in Fig. 7, that the amount of orange-colored liquid increases reaching a saturation value after seven minutes' irradiation, may be explained by the formula 10. Using this formula the parameter was estimated as follows; B is 5×10^{-2} sec.$^{-1}$, then k_5 calculated from Eq. 12, is 10^{14} cc./mol. sec. which is a reasonable value considering that the polymerization proceeds with a small amount of activation energy.

In Fig. 6, if we consider that the difference between the production of acetylene and the total pressure-increase is equal to the production of polymer, then the rate of production is zero at the beginning of the irradiation and becomes constant after a sufficient time later. This trend of polymer production can be quantitatively explained by Eq. 14.

The electronic states of mercury atom and cyclo-octatetraene molecule are shown in Fig. 13, in which the singlet states are

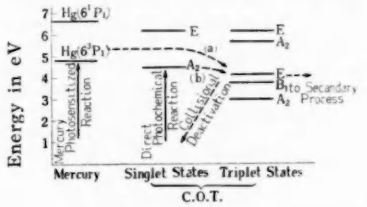

Fig. 13. Electronic states of mercury and C. O. T.

inferred from the spectroscopic data[1,4]. For the triplet states, the values from the molecular orbital calculation were used because of lack of the experimental data[2,7]. Some ambiguity is involved, however, in the determination of the assignment of those states.

In the case of the mercury photosensitized reaction, it may be considered that the reaction proceeds by path a); on the other hand in the case of the direct photochemical reaction, by path b). From the similarity of the reaction products and of the quantum yield, it may be considered that there is a cross between these states through which the reaction takes place.

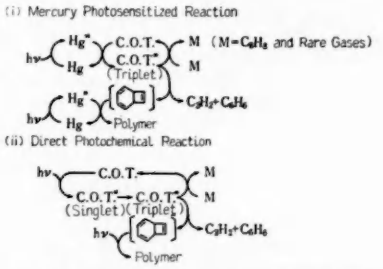

Fig. 14. Schematic representation of the mercury photosensitized and direct photochemical reactions of cyclo-octatetraene.

13) A. B. Callear and J. C. Robb, *Discussion Faraday Soc.*, No. **17**, 21 (1954).

The whole process of the reactions, mercury photosensitized as well as direct photochemical, are schematically represented in Fig. 14. Both the reactions involve the same kinds of process, i. e. the excitation of cyclo-octatetraene, the deactivation and the decomposition of the excited cyclo-octatetraene, and the polymerization process through the orange-colored liquid as intermediate.

Although the bicyclo form as an isomer of cyclo-octatetraene has not been isolated, the bicyclo forms of several derivatives of cyclo-octatetraene show ultraviolet spectra similar to those of the present orange-colored liquid[14], and this variation has been used by Reppe as an intermediate of the reaction of cyclo-octatetraene[15].

Further discussion on the present problem, however, would be largely speculative and would require much more detailed experimental result.

Summary

The reaction products of both the mercury photosensitized reaction and the direct photochemical reaction are the same, i. e. acetylene, benzene, orange-colored liquid (presumably bicyclo form of C_8H_8), polymer and a trace of styrene; the non-condensable products at liquid nitrogen temperature such as hydrogen and methane were not detected.

A quantitative experiment has been made on the decomposition reaction, in which cyclo-octatetraene shows a similar behavior to ethylene in the pressure dependence of the quantum yield. The quantum yields of the decomposition are of the same magnitude in both the mercury photosensitized and the direct photochemical reaction. The result shows that the two reactions proceed via the same excited state (probably triplet), directly or indirectly.

An investigation has also been made on the polymerization reaction, for which the total pressure change and the absorption spectrum of the reaction products have been examined in the course of the reaction. It is concluded that the polymerization takes the place via orange-colored liquid as an intermediate.

In the study of the reaction of hydrocarbons with $Hg(6^3P_1)$ atom a great deal of evidence has now been accumulated which shows the fact that the reaction always accompanies hydrogen production. The mercury photosensitized reaction of cyclo-octatetraene is one of the rare exceptions in this generality.

Thanks are due to Professor S. Shida, Tokyo Institute of Technology, for his guidance throughout this work, also to Dr. I. Tanaka, Dr. Z. Kuri and Mr. Y. Mori for their helpful discussion, and to Mr. K. Matsuzawa and Mr. R. Matsuura, Mitsubishi Kasei Co., who have furnished the sample of cyclo-octatetraene.

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14) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 168 (1952).
15) W. Reppe et al., *Ann. Chem.*, **560**, 1 (1948).

Polymerization of Methyl Methacrylate Initiated by a Combined Action of Trichloroacetic Acid and Dimethylaniline

By Ryoichi UEHARA

(Received May 27, 1958)

The author[1] preliminarily reported that polymerization of methyl methacrylate could be initiated, even at room temperature, by a combined action of trichloroacetic acid and dimethylaniline. Neither trichloroacetic acid nor dimethylaniline alone was responsible for the initiation, but, when they were dissolved together in methyl methacrylate, the polymerization was initiated. Recently, Lal[2] and others, in their paper concerning initiating actions of saccharine amine salts for polymerization of vinyl monomers, have reported that some combinations of carboxylic acids and dimethylaniline act as initiators for methyl methacrylate. But, in their report, only a brief mention of per cent yields of polymethyl methacrylate after 1 hr., at 58.6°C, was given.

This paper presents the results of experiments about the dependence of the initial rate of polymerization of methyl methacrylate upon the concentrations of both trichloroacetic acid and dimethylaniline, and a bimolecular reaction between trichloroacetic acid and dimethylaniline to form radicals is suggested as the initial reaction of the polymerization.

Experimental

Materials.—Methyl methacrylate was washed with 5% aqueous sodium carbonate and water, then distilled with steam, dried over anhydrous sodium sulfate, and carefully distilled in oxygen-free nitrogen under reduced pressure through a fractionating column. A fraction boiling at 46°C/12 mmHg was used immediately after the distillation. Dimethylaniline was distilled under nitrogen and a fraction boiling at 110°C/12 mmHg was used. Trichloroacetic acid was prepared from chloral and nitric acid, and a fraction boiling at 196°~197°C was employed. Thiophene-free benzene was dried over anhydrous sodium sulfate and distilled. Hydroquinone was dissolved in ether, decolorized by means of active carbon, and then precipitated by adding dry benzene, m.p. 174°C.

Determination of Initial Rate of Polymerization.—Polymerization of methyl methacrylate was carried out in sealed test tubes which were 15 mm. in diameter and 10 cm. in height and made of hard glass. The test tubes were cleaned by immersing them in 1% aqueous hydrofluoric acid for 12 hr., then washed with pure water and steam, and dried. Trichloroacetic acid and dimethylaniline were dissolved separately in methyl methacrylate. Both solutions were cooled in a methanol-dry ice bath, and measured amounts of both solutions were placed in a test tube and mixed. When hydroquinone was used, it was dissolved in methyl methacrylate together with dimethylaniline. In case of solution-polymerization, benzene was added to test tubes from a burette. The volume of the contents of one test tube was limited, not to exceed 5 cc. The test tubes were flashed for 10 minutes with dry nitrogen, which had been deoxygenated according to the procedure described by Fieser[3], then evacuated to 1 mmHg, and sealed. They were kept in a cooling bath for 30 minutes in order to ensure uniformity of temperature. The polymerization was effected by shaking the test tubes in a thermostat. The time of polymerization was measured from the beginning of the shaking. The yields of the polymer were measured at intervals of 15 minutes. Two tubes were picked up for one measurement, chilled in a cooling bath, and then opened. The contents of the tube were diluted with 5 cc. of acetone and taken out. The tube was then washed with 5 cc. of acetone. The contents and the washing were combined, and poured into 200 cc. of methanol so as to precipitate the polymer formed. The precipitated polymer was collected on a glass filter, washed three times with 10 cc. of methanol, then dried to a constant weight at 50°C under reduced pressure. The average weight of the samples of polymer from the two test tubes was taken as its yield. The initial rate of polymerization was determined from a linear part of the time-conversion curve in the initial stage of the polymerization, and expressed in a unit of per cent per minute.

Results and Discussion

Fig. 1 shows the relation between the initial rate of polymerization (R) and the concentration of trichloroacetic acid ([TCA]). In this case the equimolar

1) R. Uehara, Kagaku-no-Ryoiki, **7**, 295 (1953).
2) J. Lal et al., *J. Polymer Sci.*, **24**, 81 (1957).
3) L. Fieser, "Experiments in Organic Chemistry", D. C. Heath Co., New York (1941) p. 395.

amounts of trichloroacetic acid and dimethylaniline were used. So, the dependence of the initial rate of polymerization upon the concentration of dimethylaniline ([DMA]) was the same as that of Fig. 1. From Fig. 1, it can be seen that the initial rate is linearly dependent upon the concentration of trichloroacetic acid at temperatures of 25°, 35° and 55°C, respectively.

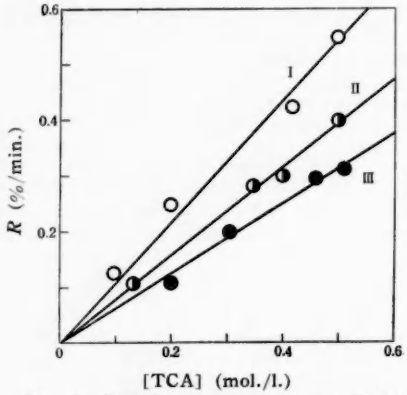

Fig. 1. Relation between R and [TCA] ([TCA]=[DMA]) I. at 55°; II, at 35°; III, at 25°C.

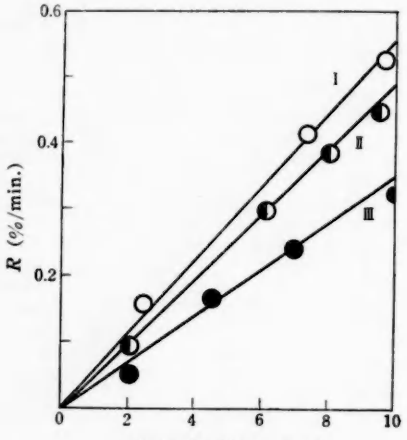

Fig. 2. Correlation of R with square-root of [DMA] at 35°C, I, [TCA]=0.50; II, [TCA]=0.42; III, [TCA]=0.21 mol./l.

When the concentration of trichloroacetic acid was held constant and that of dimethylaniline was varied, the initial rate of polymerization was linearly dependent upon the square root of the concentration of dimethylaniline, i.e., the so-called square-root dependence was observed as shown in Fig. 2. From this figure, the square-root dependence can be seen to hold for each case, in which 0.21, 0.42 and 0.50 mol./l., respectively, of trichloroacetic acid was used at 35°C. The fact that each of the straight lines in Fig. 2 is brought to a focus at the origin shows that trichloroacetic acid alone is not responsible for the initiation of polymerization.

In Fig. 3, initial rates of polymerization

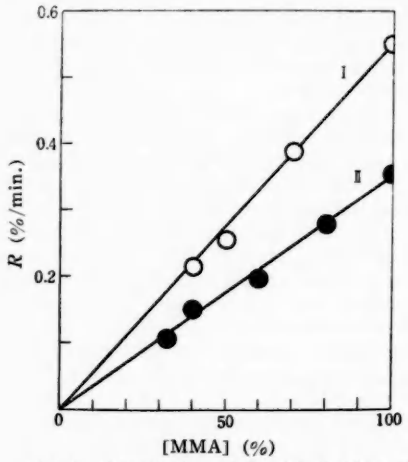

Fig. 3. Correlation of R with [MMA] at 55°C ([TCA]=[DMA]).
I, 0.50 mol./l. of TCA
II, 0.34 mol./l. of TCA

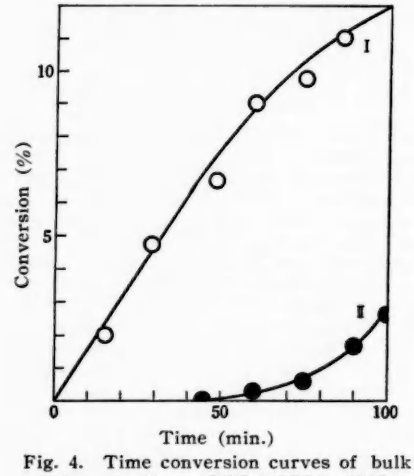

Fig. 4. Time conversion curves of bulk polymerization at 35°C ([TCA]=[DMA]=0.20 mol./l.).
I, without hydroquinone
II, with 0.026 mol./l. of hydroquinone

in benzene are plotted against the concentration of methyl methacrylate ([MMA]). Two cases, in which 0.34 and 0.50 mol./l. of trichloroacetic acid with equimolar amounts of dimethylaniline were used, are shown. The initial rate of polymerization was proportional to the concentration of methyl methacrylate.

In Fig. 4, the time-conversion curves for the bulk polymerization at 35°C, in which 0.20 mol./l. of each of trichloroacetic acid and dimethylaniline were used with or without hydroquinone, are shown. In the presence of 0.025 mol./l. of hydroquinone, a considerably long induction period was observed, therefore, it was clear that hydroquinone acted as an inhibitor for this reaction.

The relation between the initial rate and the concentration shown in Figs. 1, 2 and 3, can be represented by the following equation:

$$R = k[\mathrm{TCA}]^{1/2}[\mathrm{DMA}]^{1/2}[\mathrm{MMA}] \quad (1)$$

where k is a constant. This equation suggests a bimolecular reaction between trichloroacetic acid and dimethylaniline to form radicals as the initial reaction of the polymerization:

$$\mathrm{TCA} + \mathrm{DMA} \xrightarrow{k_1} \mathrm{R}\cdot \quad (2)$$

where k_1 is the rate constant and R· represents the radical, the chemical identity of which will be the subject for further investigation. Reaction 2 is followed by the usual series of reactions of polymerization, i. e., initiation, propagation and termination:

$$\mathrm{TCA} + \mathrm{DMA} \xrightarrow{k_1} \mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_2} \mathrm{P}_1\cdot$$

$$\mathrm{P}_m\cdot + \mathrm{M} \xrightarrow{k_3} \mathrm{P}_{m+1}\cdot$$

$$\mathrm{P}_m\cdot + \mathrm{P}_n\cdot \xrightarrow{k_4} \mathrm{P}_{m+n} \text{ or } \mathrm{P}_m + \mathrm{P}_n$$

where $\mathrm{P}_1\cdot$, $\mathrm{P}_m\cdot$, $\mathrm{P}_n\cdot$ and $\mathrm{P}_{m+1}\cdot$ represent polymer radicals, P_m, P_n and P_{m+n} polymer molecules, M is MMA, and k_2, k_3 and k_4 are rate constants, respectively, for initiation, propagation and termination. By assuming a stationary state for each of R· and P·, the following equation can be deduced for the initial rate of polymerization:

$$R = k_3(k_1/k_4)^{1/2}[\mathrm{TCA}]^{1/2}[\mathrm{DMA}]^{1/2}[\mathrm{M}] \quad (3)$$

Although the chemical identity of R· is unknown at present, equation 3 perfectly coincides with equation 1.

The rate-concentration relation represented by equation 1 or 3 is quite similar to that of Imoto[4] and others for the polymerization of vinyl monomers initiated by a combined action of benzoyl peroxide and dimethylaniline. They also postulated a bimolecular reaction between benzoyl peroxide and dimethylaniline for the initial reaction of the polymerization.

Summary

The polymerization of methyl methacrylate is initiated even at room temperature by a combined action of trichloroacetic acid and dimethylaniline. In case of bulk polymerization, the initial rate of polymerization is proportional to each of the square roots of the concentrations of trichloroacetic acid and dimethylaniline. In case of polymerization in benzene, the initial rate depends upon the concentration of methyl methacrylate. These relationships can be reasonably explained by assuming a bimolecular reaction between trichloroacetic acid and dimethylaniline to form radicals as the initial reaction of the polymerization. Hydroquinone acts as an inhibitor for this reaction.

The author thanks Professor Osamu Simamura of University of Tokyo for his kind guidance and also Mr. Tsurahide Cho, the President of Tama Kagaku Kogyo Co., for permission to undertake this work.

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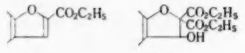
4) M. Imoto and K. Takemoto, *Chem. High Polymers (Kobunsi Kagaku)*, **12**, 120 (1955).

Synthetic Studies on the Benzofuran Derivatives. Part III. Reaction of 7-Hydroxy-8-formyl-2-methylisoflavone with Ethyl Bromomalonate and Synthesis of Furano(2',3':7,8)-2-methylisoflavone

By Takashi MATSUMOTO, Yoshiyuki KAWASE, Mutsumu NANBU and Kenji FUKUI

(Received April 16, 1958)

In previous papers of this series[1], it has been found that 2-carbethoxybenzofuran derivatives (I) or 2,2-dicarbethoxy-3-hydroxy-2,3-dihydrobenzofuran derivatives (II) were obtained by interaction of 7-hydroxy-8-formyl-flavone derivatives or *o*-hydroxybenzaldehyde derivatives with ethyl bromomalonate by means of Tanaka's method[2] for benzofuran synthesis. The present investigation was undertaken to examine a reaction of 7-hydroxy-8-formyl-2-methylisoflavone (III) with ethyl bromomalonate and to derive furano-(2',3':7,8)-2-methylisoflavone (VIII) from the condensation product (IV).



(I) (II)

III and ethyl bromomalonate were refluxed in methyl ethyl ketone or acetone in the presence of potassium carbonate. The resulting condensation product, m.p. 171~172°C, was assigned structure IV (5'-carbethoxy-furano(2',3':7,8)-2-methylisoflavone) on the basis of the following facts. The compound IV was hydrolyzed with methanolic potassium hydroxide to yield the corresponding acid V, m.p. 295~297°C (decomp.). Esterification of V with ethanol gave a compound, m.p. 171~172°C, which was identical with IV. It is of interest that the condensation reaction is analogous to the conversion of *o*-hydroxybenzaldehyde derivatives into I[1]. On hydrolytic fission with aqueous sodium hydroxide, IV gave an acid VI, m.p. 256~257°C, which had a dark violet ferric reaction; it may be benzyl 2-carboxy-4-hydroxy-5-benzofuranyl ketone. VI was esterified with ethanol to give the ester VII, m.p. 166~166.5°C, which was different from IV; it seemed to be benzyl 2-carbethoxy-4-hydroxy-5-benzofuranyl ketone, the ester of VI. The acid V was decarboxylated at 180~190° (bath temperature) into the isoflavone VIII, m.p. 187~188°C, which was thought to be furano(2',3':7,8)-2-methylisoflavone. Ramachandra Row and Seshadri[3] obtained, by an alternate route, 5'-carbethoxy-furano (2',3':7,8)-2-methylisoflavone, 5'-carboxy-furano(2',3':7,8)-2-methylisoflavone and furano(2',3':7,8)-2-methylisoflavone; the melting points of these compounds, however, differed markedly from those of the present products (IV, V and VIII) (see Table I).

TABLE I

THE MELTING POINTS OF SYNTHETIC PRODUCTS

	Our results	Results of Ramachandra Row et al.
5'-carbethoxy-furano(2',3':7,8)-2-methylisoflavone (IV)	171~172°C	225~227°C
5'-carboxy-furano(2',3':7,8)-2-methylisoflavone (V)	295~297°C (decomp.)	253~255°C (decomp.)
furano(2',3':7,8)-2-methylisoflavone (VIII)	187~188°C	95~ 96°C

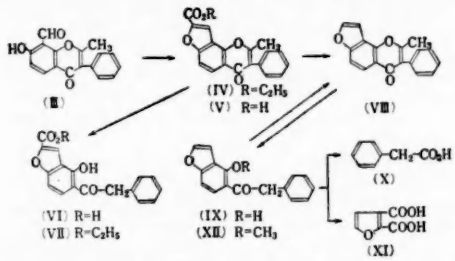
To confirm the structure of IV, V and VIII, alkaline hydrolysis of VIII was carried out to give acetic acid and a substance (IX) of colorless needles, m.p. 86~87°C, which gave a dark blue ferric reaction in ethanol. On boiling IX with a mixture of sodium acetate and acetic anhydride, an isoflavone derivative, m.p. 187~188°C, was obtained, which was identical with VIII. On oxidation with hydrogen peroxide IX gave phenylacetic acid (X), m.p. 76°C, and furan-2,3-dicarboxylic acid (XI), m.p. 220~221°C(decomp.); thus

1) Y. Kawase, T. Matsumoto and K. Fukui, This Bulletin, **28**, 273 (1955); T. Matsumoto and K. Fukui, ibid., **30**, 3 (1957).

2) S. Tanaka, *J. Am. Chem. Soc.*, **73**, 872 (1951).

3) L. Ramachandra Row and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **34A**, 187 (1951).

IX was considered to be benzyl 4-hydroxy-5-benzofuranyl ketone. To further confirm the structure of IX, its methyl ether XII, m.p. 61.5～62°C, was derived. This ether was conveniently compared with a ketone prepared from the acid chloride of karanjic acid methyl ether and dibenzyl-



cadmium (m.p. 63～63.5°C). The mixed melting point was undepressed*. VIII, IV and V were thus assigned furano(2',3':7,8)-2-methylisoflavone and 5'-carbethoxy-furano(2',3':7,8)-2-methylisoflavone and 5'-carboxy-furano(2',3':7,8)-2-methylisoflavone, respectively.

Experimental**

7-Hydroxy-8-formyl-2-methylisoflavone (III).—The aldehyde was prepared from 7-hydroxy-2-methylisoflavone by the hexamine method[3].

5'-Carbethoxy-furano(2',3':7,8)-2-methylisoflavone (IV).—A mixture of 6.5 g. of the aldehyde III, 6.1 g. of ethyl bromomalonate, 12 g. of anhydrous potassium carbonate and 230 cc. of methyl ethyl ketone was refluxed with stirring for 10 hr. in a steam-bath. After being cooled, the mixture was filtered and evaporated to dryness. Recrystallization from ethanol yielded colorless needles, which gave a negative ferric reaction (in ethanol) and also gave no 2,4-dinitrophenylhydrazone; yield 4.8 g., m.p. 171～172°C.

Anal. Found: C, 72.43; H, 4.38. Calcd. for $C_{21}H_{16}O_5$: C, 72.40; H, 4.63%.

Acetone was favorably substituted for the methyl ethyl ketone.

5'-Carboxy-furano(2',3':7,8)-2-methylisoflavone (V).—A mixture of 2.0 g. of the ester IV, 1.0 g. of potassium hydroxide and 80 cc. of methanol was heated under reflux for 1 hr. in a steam-bath. The reaction mixture was acidified with dilute sulfuric acid. After the solvent was distilled off, the residual solids were collected, washed with water and recrystallized from methanol in colorless needles, m.p. 295～297°C (decomp.), which gave a negative ferric reaction (in ethanol) and was soluble in 5% aqueous sodium hydrogen carbonate; yield 1.7 g.

Anal. Found: C, 71.23; H, 3.90. Calcd. for $C_{19}H_{12}O_5$: C, 71.25; H, 3.78%.

Esterification of V.—A mixture of 0.5 g. of the acid V, 1 cc. of concentrated sulfuric acid and 35 cc. of absolute ethanol was refluxed for 8 hr. The reaction mixture was treated in the usual manner and recrystallized from ethanol to give 0.4 g. of colorless needles, m.p. 171～172°C; the melting point was undepressed on admixture with the above sample IV, m.p. 171～172°C.

Anal. Found: C, 72.28; H, 4.82. Calcd. for $C_{21}H_{16}O_5$: C, 72.40; H, 4.63%.

Fission of IV.—A mixture of 2.3 g. of the ester IV and 150 cc. of 5% aqueous sodium hydroxide was heated in a steam-bath with occasional shaking for 3 hr. After the reaction mixture was filtered and acidified with sulfuric acid, the precipitates were collected and washed with water. Recrystallization from methanol yielded benzyl 2-carboxy-4-hydroxy-5-benzofuranyl ketone VI, m.p. 256～257°C in colorless needles, which gave a dark violet ferric reaction (in ethanol); yield 1.3 g.

Anal. Found: C, 69.21; H, 4.06. Calcd. for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08%.

A mixture of 0.5 g. of VI, 1 cc. of concentrated sulfuric acid and 35 cc. of absolute ethanol was refluxed for 8 hr. The reaction mixture was worked up in the usual manner and recrystallized from ethanol to give colorless needles of benzyl 2-carbethoxy-4-hydroxy-5-benzofuranyl ketone (VII), which had a brown ferric reaction (in ethanol); yield 0.4 g., m.p. 166～166.5°C.

Anal. Found: C, 70.23; H, 5.04. Calcd. for $C_{19}H_{16}O_5$: C, 70.36; H, 4.98%.

Furano(2',3':7,8)-2-methylisoflavone(VIII).—A mixture of 6.0 g. of V, 3.5 g. of copper powder and 180 cc. of quinoline was heated with stirring in an atmosphere of nitrogen for ca. 30 min. at 180～190° (bath temperature) until evolution of carbon dioxide ceased. After being cooled, the copper powder was filtered off, and the solution was acidified with dilute sulfuric acid. The precipitates thus formed were collected, washed with aqueous sodium hydrogen carbonate and then with water. Recrystallization from ethyl acetate gave colorless needles, which had a negative ferric reaction (in ethanol); yield 3.4 g., m.p. 187～188°C.

Anal. Found: C, 78.44; H, 4.46. Calcd. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%.

Fission of VIII.—A mixture of 2.0 g. of VIII, 4.0 g. of potassium hydroxide and 110 cc. of ethanol was heated for 4 hr. in a steam-bath. After the solvent was evaporated, the residue was mixed with water and acidified with dilute sulfuric acid. The resulting precipitates were collected, washed with water and recrystallized from ethanol as colorless needles of benzyl 4-hydroxy-5-benzofuranyl ketone (IX), which had a dark blue ferric reaction (in ethanol); yield 1.6 g., m.p. 86～87°C.

Anal. Found: C, 76.23; H, 5.02. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80%.

The mother liquor, which was freed from the above precipitates, was steam-distilled and the

* The details of the synthesis of this ketone (XII) will be given in the following paper.

** All the melting points were uncorrected.

distillate was neutralized with 0.1 N sodium hydroxide solution. A part of the neutralized solution (0.0025 mole) was concentrated to ca. 2 cc. in vacuo, and mixed with 0.7 g. of a solution of *p*-bromophenacyl bromide in 100 cc. of ethanol. The mixture was refluxed for 1 hr. in a steam-bath, the solvent, removed, and water was added. The precipitates obtained were collected, washed with water and recrystallized from aqueous ethanol to form colorless plates; yield 0.3 g., m.p., 84~85°C. The melting point was undepressed on admixture with an authentic sample of *p*-bromophenacyl ester of acetic acid, m.p. 84~85°C.

Anal. Found: C, 46.99; H, 3.79. Calcd. for $C_{10}H_9O_3Br$: C, 46.72; H, 3.53%.

Reactions of Benzyl 4-Hydroxy-5-benzofuranyl Ketone (IX).—*a*).—A mixture of 0.35 g. of the ketone IX, 2.0 g. of anhydrous sodium acetate and 10 cc. of acetic anhydride was refluxed for 12 hr. in an oil bath. The excessive acetic anhydride was removed in vacuo, the residue was made alkaline with 5% aqueous sodium hydroxide and then extracted with ether. The ethereal solution was washed with 5% aqueous sodium hydroxide, then with water, dried over anhydrous sodium sulfate and evaporated. The crude residue was recrystallized from ethyl acetate in colorless needles, which had a negative ferric reaction (in ethanol); yield 0.15 g., m.p. 187~188°C (alone or mixed with VIII).

b) *Oxidation.*—On a steam-bath 1.0 g. of IX was heated with 200 cc. of 2.5% aqueous potassium hydroxide until a clear solution was obtained, which was cooled to room temperature, and 50 cc. of hydrogen peroxide solution (8%) was added slowly. Then the reaction mixture was kept for 18 hr. at room temperature and then heated for 6 hr. in a steam-bath to decompose the excessive hydrogen peroxide. The solution was acidified with dilute hydrochloric acid and evaporated in vacuo to dryness and then extracted continuously with ether for 17 hr. The ethereal solution was extracted with 5% aqueous sodium hydrogen carbonate. This solution was made slightly acidic with dilute hydrochloric acid and then made slightly alkaline with dilute aqueous ammonia solution, then a solution of 1.0 g. of calcium chloride was added and the precipitates formed were filtered off. The filtrate was acidified with dilute hydrochloric acid and evaporated to ca. 20 cc. in vacuo. After cooling, the crude phenylacetic acid was removed by filtration. The mother liquor was continuously extracted with ether for 17 hr. The ethereal extracts, upon evaporation, yielded a mixture of phenylacetic acid and furan-2,3-dicarboxylic acid (XI), which were separated by trituration with cold chloroform. The suspended solid was collected. Recrystallization from acetic acid gave XI in colorless needles, m.p. 220~221°C (decomp.) which had a negative ferric reaction (in ethanol); yield 0.1 g. This product did not depress the melting point of authentic furan-2,3-dicarboxylic acid[4] made from karanjic acid.

Anal. Found: C, 46.26; H, 2.90. Calcd. for $C_6H_4O_5$: C, 46.17; H, 2.58%.

Evaporation of the chloroform layer yielded crude phenylacetic acid. The combined crude phenylacetic acid was recrystallized from water in colorless plates; yield 0.15 g., m.p. 76°C. The melting point was undepressed on admixture with an authentic sample of phenylacetic acid, m.p. 76°C.

c) *Methylation.*—A mixture of 1.0 g. of IX, 1.0 g. of anhydrous potassium carbonate and a solution of 1 cc. of dimethyl sulfate in 20 cc. of anhydrous acetone was refluxed for ca. 20 hr. in a steam-bath. The precipitates were filtered off, the acetone was removed and the residue washed with 5% dilute sodium hydroxide and then with water. Recrystallization from ethanol gave colorless plates, m.p. 61.5~62°C, which had a negative ferric reaction (in ethanol); yield 0.7 g. The melting point of this compound was undepressed on admixture with synthetic sample m.p. 63~63.5°C, which was obtained from the acid chloride of karanjic acid methyl ether and dibenzylcadmium.*

Anal. Found: C, 76.98; H, 5.88. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30%.

Summary

5'-Carbethoxy-furano(2',3' : 7,8)-2-methylisoflavone (IV) was obtained from 7-hydroxy-8-formyl-2-methylisoflavone (III) and ethyl bromomalonate by Tanaka's method for benzofuran synthesis. The condensation product IV was hydrolyzed to give the free acid V, which was decarboxylated in quinoline with copper powder to yield furano(2',3' : 7,8)-2-methylisoflavon (VIII). The structures of the condensation product and its derivatives were discussed.

We are grateful to the Institute of Agricultural Chemistry, Faculty of Agriculture, Kyoto University for microanalyses.

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4) B. L. Manjunath, A. Seetharamiath and S. Siddappa, *Ber.*, **72B**, 93 (1939).

Synthetic Studies on the Benzofuran Derivatives. Part IV. A New Synthesis of Benzyl 2-Methoxyphenyl Ketones and a Synthesis of Benzyl 4-Methoxy-5-benzofuranyl Ketone (Benzyl O-Methyl-karanjyl Ketone)

By Yoshiyuki KAWASE, Teruo FUJIMOTO and Kenji FUKUI

(Received April 16, 1958)

In the preceding paper[1] of this series, the preparation of furano (2′, 3′ : 7, 8)-2-methylisoflavone (I), m.p. 187~188°C, was described, but as mentioned already, the melting points of it and the related compounds were quite different from those of the compounds reported by Row et al.[2]

Now, to further confirm the structure of the expected benzyl 4-hydroxy-5-benzofuranyl ketone (benzyl karanjyl ketone) (II) which was obtained by alkaline hydrolysis[1] of I, a synthesis of II or its methyl ether III by a different method from that of Row et al. 's[2] was attempted; III was prepared by the interaction of 4-methoxy-5-benzofuranoyl chloride (*O*-methyl-karanjic acid chloride) (IV) and dibenzylcadmium.

The usual preparative methods of benzyl 2-hydroxyphenyl ketones are: a) the interaction of phenols with phenylacetonitriles or phenylacetic acids or phenylacetyl chlorides, according to the Hoesch, Nencki, and Friedel-Crafts reaction, respectively; b) the rearrangement of phenyl phenylacetates according to the Fries reaction. In these reactions, however, the position of the phenylacetyl group which enters into the phenol nucleus is restricted, and thus the preparation of the hydroxyketone II from 4-hydroxybenzofuran (karanjol) by these methods is unsuccessful[3].

A new synthetic route to benzyl 2-hydroxyphenyl ketones was recently reported by one of the authors[4], which involves the ester condensation of methyl 2-methoxybenzoates with phenylacetonitriles followed by hydrolysis. But an attempted synthesis, by this method, of II from methyl 4-methoxy-5-benzofuranoate (methyl *O*-methyl-karanjate) and phenylacetonitrile resulted in failure because of the abortive ester condensation.

The preparation of benzyl 2-methoxyphenyl ketones has been described by Tiffeneau et al.[5], but this method which involves the Grignard reaction and the Tiffeneau rearrangement is unfavorable in the present case.

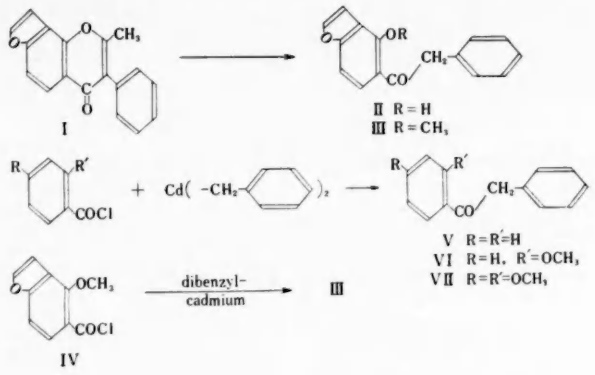
Therefore, another method of synthesis for benzyl 2-methoxyphenyl ketones was explored. By this means it was found that a reaction of 2-methoxybenzoyl chlorides with dibenzylcadmium in anhydrous benzene was feasible. A reaction of benzoyl chloride or 2-methoxybenzoyl chloride or 2,4-dimethoxybenzoyl chloride with dibenzylcadmium gave phenyl benzyl ketone (deoxybenzoin) (V), benzyl 2-methoxyphenyl ketone (VI), and benzyl 2,4-dimethoxyphenyl ketone (VII), respectively. A small amount of 1,2-diphenyl ethane was obtained as a by-product from the forerun of the distillates.

By the interaction of IV and dibenzylcadmium in anhydrous benzene, the desired methoxy-ketone (III) was obtained in colorless crystals, m.p. 63~63.5°C, which was identical with the sample reported in the preceding paper.

Experimental[6]

Phenyl Benzyl Ketone (Deoxybenzoin) (V).—The following reaction was carried out under a stream of dry nitrogen gas with stirring. To a solution of Grignard reagent prepared from 4.2 g. of freshly distilled benzyl bromide and 0.6 g. of magnesium in 100 cc. of anhydrous ether was carefully added 2.4 g. of powdered anhydrous cadmium chloride at room temperature, and the mixture was refluxed for 1 hr. Most of the ether was distilled off, 100 cc. of anhydrous benzene

1) Part III by T. Matsumoto, Y. Kawase, M. Nanbu and K. Fukui, This Bulletin, **31**, 688 (1958).
2) L. R. Row and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **34A**, 187 (1951); *Chem. Abstr.*, **47**, 12374 (1953).
3) B. L. Manjunath, A. Seetharamiah and S. Siddappa, *Ber.*, **72**, 93 (1939); S. H. Harper, *J. Chem. Soc.*, **1942**, 593; A. Seetharamiah, ibid., **1948**, 894.
4) Y. Kawase, This Bulletin, **31**, 390 (1958).
5) J. Lévy and R. Pernot, *Bull. soc. chim.*, **49**, 1730 (1931); M. Tiffeneau, A. Oryékhov and M. Roger, ibid., **49**, 1757 (1931).
6) Melting and boiling points are uncorrected.



was added, and the remaining ether was distilled off. Then a solution of 5 g. of benzoyl chloride in 50 cc. of anhydrous benzene was added slowly at room temperature, and the mixture was refluxed for ca. 4 hr. The cooled reaction mixture was shaken with 200 cc. of dilute sulfuric acid, the organic portion separated, washed with water, and then warmed with 5% aqueous sodium hydroxide with shaking for a while to decompose the excess of chloride. The benzene solution which had separated was washed with water, dried, and the solvent was distilled off. The residual oily product was distilled, b.p. 120~180°C/4 mm. (bath temperature); yield 2.3 g. A sample of V for analysis was obtained from a higher-boiling fraction by crystallization from ethanol in colorless needles, m.p. 52~53°C, which was identical with an authentic sample[7]. V which was contained in the distillate was confirmed through its 2,4-dinitrophenylhydrazone, m.p. 197~197.5°C, identical with an authentic sample, m.p. 197~198°C; reported b.p. 160°C/5 mm., m.p. 55~56°C[7] and m. p. of 2, 4-dinitrophenylhydrazone 202~204°C[8].

Anal. of V. Found: C, 85.41; H, 6.35. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16%.

From the mother liquor of 2,4-dinitrophenylhydrazone, 1,2-diphenylethane was obtained by distillation. Crystallization from ethanol gave colorless crystals, m.p. 51~52°C, which was identical with an authentic sample[9]; yield 0.4 g.; reported b.p. 158°C/10 mm. and m.p. 51°C[9].

Benzyl 2-Methoxyphenyl Ketone (VI).—By the procedure described before, dibenzylcadmium was prepared from 2.3 g. of cadmium chloride and benzylmagnesium bromide (from 3.5 g. of benzyl bromide and 0.5 g. of magnesium) in 100 cc. of anhydrous benzene. The reagent was allowed to react with a solution of 5 g. of 2-methoxybenzoyl chloride in 50 cc. of benzene; the chloride was prepared from 2-methoxybenzoic acid and excessive thionyl chloride, b.p. 145~146°C/25 mm. After the same treatment as described before, two fractions were obtained by distillation: (a) b.p. 90~150°C/4 mm., yield 0.5 g.; (b) b.p. 163~164°C/4 mm., yield 1.5 g. The lower boiling fraction became solid on standing, which on recrystallization from ethanol yielded a compound, m.p. 50~51°C, identical with an authentic sample of 1,2-diphenylethane. The higher boiling fraction which remained unsolidified consisted of VI, which was ascertained from its 2,4-dinitrophenylhydrazone, m.p. 162~163°C (from ethanol), identical with the other sample[4]. Reported boiling points of VI are 202~204°C/14 mm.[5], 198~202°C/14 mm.[5] and 130~131°C/0.001 mm.[4], and the melting point of the 2,4-dinitrophenylhydrazone 163~164°C[4].

Benzyl 2,4-Dimethoxyphenyl Ketone (VII).—The preparation followed the same method as in the above case. 2,4-Dimethoxybenzoyl chloride was employed in place of 2-methoxybenzoyl chloride; the chloride was prepared by heating an excess of thionyl chloride with 7 g. of 2,4-dimethoxybenzoic acid at 50° for twenty minutes, the excess of thionyl chloride removed in vacuo, and the crude chloride was used. The product was distilled at 160~180°C/4 mm. (bath temperature) to give colorless oil, yield 2 g., which was crystallized from ethanol in colorless needles, m.p. 46.5~47°C, identical with an authentic sample prepared by methylation of benzyl 2,4-dihydroxyphenyl ketone. The 2,4-dinitrophenylhydrazone, m.p. 194~195°C (from ethanol-ethyl acetate), was identical with an authentic sample; reported m.p. of VII 47~48°C[5].

Anal. of VII. Found: C, 74.90; H, 6.40. Calcd. for $C_{16}H_{16}O_3$: C, 74.96; H, 6.30%.

From the forerun in the case of the distillation (0.5 g.), 1,2-diphenylethane was obtained, m.p. 52~53°C.

Benzyl 4-Methoxy-5-benzofuranyl Ketone (III).—*O*-Methyl-karanjic acid (4-methoxy-5-benzofuranoic acid)[10] was prepared from karanjic

7) C. F. H. Allen and W. E. Barker, *Org. Synth.*, **Coll. Vol. II**, 156 (1943).
8) M. S. Newman and W. M. Edwards, *J. Am. Chem. Soc.*, **76**, 1840 (1954).
9) T. Reichstein and R. Oppenauer, *Helv. Chim. Acta*, **16**, 1377 (1933).
10) T. R. Seshadri and V. Venkateswalu, *Proc. Indian Acad. Sci.*, **13A**, 404 (1941), *Chem. Abstr.*, **35**, 7961 (1941); B. L. Manjunath and A. Seetharamiah, *J. Mysore Univ.*, **Sec. B. 2**, 3, 19 (1941), *Chem. Abstr.*, **36**, 1935 (1942).

acid[11] by refluxing it with dimethyl sulfate and potassium carbonate in acetone for 15 hr. The product was subjected to alkaline hydrolysis, and the acid obtained (3 g.) was warmed with excessive thionyl chloride at 50°C for 20 min., and the excessive thionyl chloride was removed in vacuo. Benzene (50 cc.) was added to the residue, and the traces of thionyl chloride, together with benzene, were removed by warming to dryness in vacuo. A solution of the crude chloride IV[10] in 50 cc. of anhydrous benzene was added to a suspension of dibenzylcadmium (prepared from 2 g. of cadmium chloride and benzylmagnesium bromide (from 2.7 g. of benzyl bromide and 0.4 g. of magnesium)) in 100 cc. of anhydrous benzene. After the same treatment as described before, the product was distilled at 150~180°C/0.003 mm. (bath temperature) to give colorless oil, yield 1.1 g., which was crystallized from ethanol in colorless crystals, m.p. 63~63.5°C, and identical with the sample reported in the preceding paper. It gave 2,4-dinitrophenylhydrazone of m.p. 227~228°C (from ethanol-ethyl acetate).

Anal. of III. Found: C, 76.23; H, 5.41. Calcd. for $C_{17}H_{14}O_3$: C, 76.66; H, 5.30%.

From the forerun in the case of the distillation (0.3 g.), 1,2-diphenylethane was obtained, m.p. 51~52°C.

11) R. T. Foster and A. Robertson, *J. Chem. Soc.*, **1948**, 115.

We are grateful to the Institute of Agricultural Chemistry, Faculty of Agriculture, Kyoto University for microanalyses.

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Synthetic Studies on the Benzofuran Derivatives. Part V. Synthesis of Furano(2′, 3′ : 7, 8)-isoflavone

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(Received April 16, 1958)

In a previous paper[1], furano (2′, 3′ : 7, 8)-2-methylisoflavone (I) was obtained by Tanaka's method[2] for benzofuran synthesis. It is of interest to prepare some furano-isoflavone derivatives and compare their behavior with that of the 2-methyl compounds in a number of reactions.

The present paper describes the synthesis of furano(2′, 3′ : 7, 8)-isoflavone (III). For this purpose two possible methods have been explored. The first method was to complete the isoflavone structure using a suitable coumarone derivative, benzyl 4-hydroxy-5-benzofuranyl ketone (II), as the starting material. The second one consisted in the introduction of a furan nucleus into an isoflavone skeleton (Tanaka's method[2]).

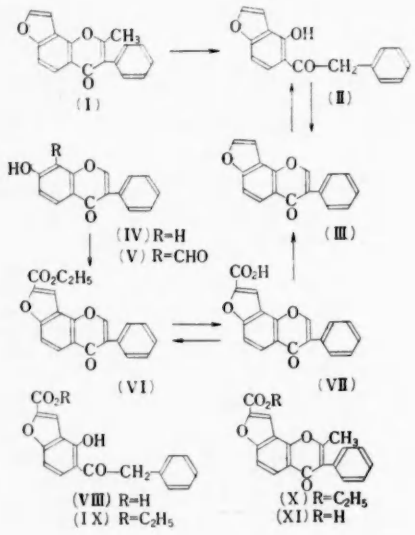
By means of the first method, II[1] (benzyl karanjyl ketone), which was fairly easily obtained as the product of hydrolysis of I, led to III, m.p. 152~152.5°C, on condensation with ethyl orthoformate in pyridine containing a little piperidine (method of Sathe and Venkataraman[3]).

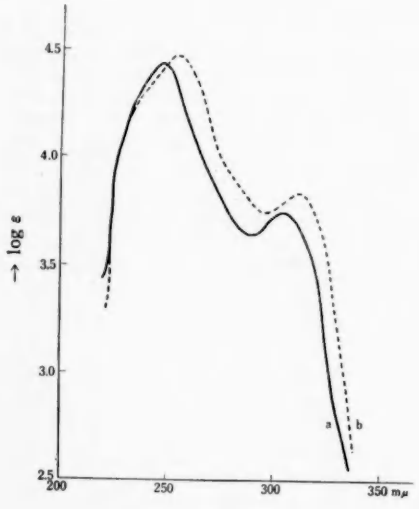
As regards the second method, the application to the present case presented more difficulties than in the case of the synthesis of the 2-methyl derivative (I). The starting material was 7-hydroxyisoflavone (IV) which readily yielded the corresponding 8-aldehyde (V) by the hexamine method. The next step which involved the condensation with bromomalonic ester to 5′-carbethoxy-furano-(2′, 3′ : 7, 8)-isoflavone (VI) also proceeded smoothly.

The reaction of VI with hot aqueous sodium hydroxide brought about a conversion into benzyl 2-carboxy-4-hydroxy-5-benzofuranyl ketone (VIII), which was identical with the sample obtained[1] by hydrolysis of 5′-carbethoxy-furano(2′, 3′ : 7, 8)-2-methylisoflavone (X). By the action of ethanolic sodium hydroxide, 5′-carboxy-furano(2′, 3′ : 7, 8)-isoflavone (VII) could be obtained together with a small quantity of benzyl 2-carbethoxy-4-hydroxy-5-benzofuranyl ketone (IX), which was identical with the sample produced[1] by esterification

1) T. Matsumoto, Y. Kawase, M. Nanbu and K. Fukui, This Bulletin, **31**, 688 (1958).
2) S. Tanaka, *J. Am. Chem. Soc.*, **73**, 872 (1951).
3) V. R. Sathe and K. Venkataraman, *Current Sci. (India)*, **18**, 378 (1949), *Chem. Abst.*, **44**, 8916 (1950).

of VIII. When VI was refluxed with aqueous sodium carbonate in acetone, VII was also obtained together with a small quantity of VIII. While X gave corresponding acid XI in a satisfactory yield[1], saponification of the ester VI to VII was of lower yield. This difference may be due possibly to the greater reactivity of an isoflavone ring owing to the absence of the 2-methyl group. VII was decarboxylated into III, m.p. 151~151.5°C, which was identical with the isoflavone prepared by the ethyl orthoformate method. The ultraviolet spectrum of III almost agreed with that of I (Fig. 1). Hydrolytic decomposition of III gave II, which was identical with the sample obtained[1] from I.





→ Wave length

Fig. 1. Ultraviolet absorption of the isoflavone in ethanol.
(a) Furano(2', 3':7, 8)-2-methylisoflavone(I)
(b) Furano(2', 3':7, 8)-isoflavone(III)

Experimental*

7-Hydroxy-8-formyl-isoflavone(V).—A mixture of 7-hydroxy-isoflavone (IV) (1.5 g.), hexamine (8 g.) and glacial acetic acid (25 cc.) was heated in a steam-bath for 6 hr. The resulting hot reddish brown liquid was treated with hydrochloric acid (1:1, 24 cc.) and again heated in a steam-bath for ca. 5 min. After dilution with water (40 cc.) it was allowed to stand overnight. The yellow precipitates were collected, washed with water and dried. The dry solids were extracted twice with hot benzene (25 cc.) and the residue rejected. The benzene solution was evaporated, leaving V which, on repeated purification from ethanol, formed colorless needles, m.p. 197~198°C, which gave a red ferric reaction (in ethanol); yield 0.6 g.

Anal. Found: C, 72.01; H, 4.01. Calcd. for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79%.

5'-Carbethoxy-furano(2', 3':7,8)-isoflavone (VI).—V (3 g.) was treated with ethyl bromomalonate (3.3 g.) and anhydrous potassium carbonate (13.5g.) in anhydrous acetone (150cc.). After being refluxed for 10.5 hr., the mixture was filtered and evaporated to dryness. The residue was collected, and washed with water. Recrystallization from ethanol gave colorless needles, which had a negative ferric reaction (in ethanol); yield 2.5 g., m.p. 172~173°C.

Anal. Found: C, 71.48; H, 4.31. Calcd. for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22%.

Hydrolysis of 5'-Carbethoxy-furano(2', 3':7,8)-isoflavone (VI).—*a) Hydrolysis by aqueous sodium hydroxide.*—A mixture of VI (0.6 g.) and 5% aqueous sodium hydroxide (50 cc.) was heated in a steam-bath for 3 hr. After the reaction mixture was acidified with dilute sulfuric acid, the precipitates were collected, washed with water and crystallized from ethanol to yield colorless needles (0.5 g.), m.p. 256~257°C, which gave a dark violet ferric reaction in ethanol and was soluble in 5% aqueous sodium hydrogen carbonate. The mixed melting point test showed the identity of the above compound with benzyl 2-carboxy-4-hydroxy-5-benzofuranyl ketone (VIII), m.p. 256~257°C, obtained[1] from 5'-carbethoxy-furano (2', 3':7, 8)-2-methylisoflavone (X).

b) Hydrolysis by aqueous sodium carbonate-acetone.—A mixture of VI (0.5 g.), acetone (20 cc.) and 5% aqueous sodium carbonate (20 cc.) was heated under reflux in a steam-bath for

* All the melting points were uncorrected.

4 hr.; a great amount of the precipitates was formed during the reaction. Acetone was evaporated in vacuo, the reaction mixture was diluted with water (20 cc.) and filtered. The precipitates, perhaps sodium salt of the acid VII, were heated with dilute hydrochloric acid for a few minutes; the deposits were collected and washed with water. Recrystallization from glacial acetic acid gave 5'-carboxy-furano(2', 3':7, 8)-isoflavone (VII) in microcrystals. This had a negative ferric reaction in ethanol and produced carbon dioxide and sparingly soluble sodium salt with 5% aqueous sodium hydrogen carbonate; yield 0.2 g., m.p. 283°C (decomp.). The analytical sample was further dried at 120°C over phosphoruspentoxide for 4 hr. in vacuo.

Anal. Found: C, 66.77; H, 3.63. Calcd. for $C_{18}H_{10}O_5 \cdot H_2O$: C, 66.67; H, 3.70%.

VII afforded VI on esterification with ethanol in the presence of sulfuric acid, m.p. and mixed m.p. 172~173°C. VII was converted into VIII, m. p. 252~253°C, by further hydrolysis with aqueous sodium hydroxide.

The mother liquor of the sodium salt of VII was acidified with dilute hydrochloric acid and the precipitates obtained were crystallized from ethanol to yield VIII (0.1 g.), m.p. 251°C. This gave a dark violet ferric reaction (in ethanol).

c) Hydrolysis by ethanolic sodium hydroxide.—A hot solution of VI (0.5 g.) in ethanol (50 cc.) was added to a hot solution of sodium hydroxide (0.1 g.) in ethanol (20 cc.) and refluxed for 1 hr. After being cooled, the white precipitates were collected and treated with hot dilute hydrochloric acid. Recrystallization from glacial acetic acid gave microcrystals, which had a negative ferric reaction (in ethanol); yield 0.25 g., m.p. 280°C (decomp.). The mixed melting point test proved the compound to be identical with VII.

The filtrate, which was separated from the above precipitates, was acidified with diluted hydrochloric acid and diluted with water until it became turbid. The deposits were collected and recrystallized from ethanol to give colorless needles, which had a brown ferric reaction in ethanol and were insoluble in 5% aqueous sodium hydrogen carbonate; yield 0.1 g., m.p. 163~164°C.

Anal. Found: C, 70.35; H, 4.83. Calcd. for $C_{19}H_{16}O_5$: C, 70.36; H, 4.98%.

The mixed melting point test proved the compound to be identical with benzyl 2-carbethoxy-4-hydroxy-5-benzofuranyl ketone (IX), m.p. 166~166.5°C, which was obtained[1] by esterification of VIII. IX produced the acid VIII, m.p. 250~252°C, on further hydrolysis with aqueous sodium hydroxide.

Furano (2', 3' : 7, 8) - isoflavone (III). — *a)* Benzyl 4-hydroxy-5-benzofuranyl ketone (II) (0.7 g.), which was prepared from furano(2', 3':7, 8)-2-methylisoflavone[1], was heated under reflux with freshly distillated ethyl orthoformate (2 g.) in anhydrous pyridine (8 cc.) containing one drop of piperidine for 8 hr. After the solution was cooled and acidified with dilute sulfuric acid, the precipitates were collected, washed with 5% aqueous sodium hydroxide and then with water. Recrystallization from ethanol gave colorless needles, which had a negative ferric reaction (in ethanol); yield 0.3 g., m.p. 152~152.5°C.

Anal. Found: C, 77.64; H, 4.10. Calcd. for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84%.

b) A mixture of VII (0.8 g.), copper powder (0.5 g.) and quinoline (35 cc.) was heated while stirred in an atmosphere of nitrogen for ca. 40 min. at 180~190°C (bath temperature) until evolution of carbon dioxide ceased. After being cooled and freed from copper powder, quinoline was removed by steam distillation. Dilute sulfuric acid was poured into the remainder and the precipitates were collected. After being treated with 5% aqueous sodium hydrogen carbonate and washed with water, the solids were recrystallized from ethyl acetate and then ethanol to give the isoflavone (III) (0.5 g.) in colorless needles, m.p. 151~151.5°C. This had a negative ferric reaction (in ethanol). The melting point was undepressed on admixture with the sample in the case *a*).

Hydrolytic Fission of the Isoflavone (III) to II.—A mixture of III (1 g.), potassium hydroxide (1.8 g.) and ethanol (70 cc.) was heated under reflux for 3 hr. in a steam-bath. After the solvent was evaporated, the residue was mixed with water (50 cc.) and acidified with dilute sulfuric acid. The precipitates were collected and washed with water. Recrystallization from ethanol gave colorless needles which had a dark blue ferric reaction (in ethanol); yield 0.8 g., m.p. 85~86°. The melting point was undepressed on admixture with II, m.p. 86~87°C, which was obtained[1] from furano(2', 3':7, 8)-2-methylisoflavone (I).

Summary

1) Furano(2', 3' : 7,8)-isoflavone (III) was prepared from benzyl 4-hydroxy-5-benzofuranyl ketone (II) and ethyl orthoformate.

2) 7-Hydroxy-8-formyl-isoflavone (V) was obtained from 7-hydroxy-isoflavone (IV) by the hexamine method. 5'-Carbethoxy-furano(2', 3' : 7, 8)-isoflavone (VI) was prepared from 7-hydroxy-8-formylisoflavone (V) and ethyl bromomalonate by Tanaka's method for benzofuran synthesis. The ester VI was hydrolyzed to the free acid VII and then decarboxylated in quinoline with copper powder to the isoflavone III.

We are grateful to the Institute of Agricultural Chemistry, Faculty of Agriculture, Kyoto University, for microanalyses and to Miss M. Fukushima for her helpful assistance.

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*Studies on Organic Peroxides. IV. Polymerization of Vinyl Acetate in Benzoyl Peroxide-Fe(II)-Benzoin Redox System**

By Shigeo HASEGAWA, Nishio HIRAI, Norio NISHIMURA and Tsugio KAWANO

(Received May 21, 1958)

Polymerization of vinyl monomers in the redox systems of non-aqueous solution has been widely studied by W. Kern et al.[1]. According to them, in the redox system which consists of ferrous ion, benzoin and benzoyl peroxide, the following reactions take place by the Haber-Weiss one-electron transfer mechanism[2], in which the ferric ion is reduced to the ferrous by benzoin acting as reductant:

$$P + Fe^{2+} \xrightarrow{k_1} RCOO\cdot + RCOO^- + Fe^{3+} \quad (1)$$

$$BzH_2 + 2Fe^{3+} \xrightarrow{k_2} 2Fe^{2+} + Bz + 2H^+ \quad (2)$$

where P, BzH_2, Bz and RCOO· represent benzoyl peroxide, benzoin, benzil and benzoate radical, respectively; k_1 and k_2 are the rate constants of the reactions 1 and 2, respectively.

Ukida[3] has ascertained the reaction 2 polarographically, and has also found that the rate of polymerization of vinyl acetate in this redox system was appreciably affected by the amount of ferrous salt added. The reaction 2 may reasonably be assumed to take place in two steps as follows:

$$BzH_2 + Fe^{3+} \xrightarrow{k_2} Fe^{2+} + BzH\cdot + H^+$$

$$BzH\cdot + Fe^{3+} \xrightarrow{\text{rapid}} Fe^{2+} + Bz + H^+ \quad (2')$$

No kinetic considerations seem, however, to have been proposed about the redox polymerization in this system.

In this paper, the dependence of the rate and the extent of polymerization of vinyl acetate on the initial concentration of the ferrous ion which was added was studied by following the course of the rate of polymerization dilatometrically, to make clear the mechanism of the ferrous-ion catalysed decomposition of benzoyl peroxide in ethanol.

Experimental

Reagents. — In order to remove aldehydes, commercial vinyl acetate was washed with 5% sodium bisulfite solution, followed by washing with water, then the monomer was dried with calcium chloride, and stored in the dark after distillation. Just before use, the monomer was distilled once more and the fraction at 71.5~73°C was used. Ferrous chloride ($FeCl_2 \cdot 4H_2O$) was crystallized from iron powder and hydrochloric acid, and stored in carbon dioxide atomosphere to prevent oxidation. Ethanol was repeatedly distilled with calcium oxide to remove water. Benzoyl peroxide and benzoin were prepared and recrystallized in the usual manner.

Procedure. — Ethanolic solution of ferrous chloride and vinyl acetate solution containing benzoyl peroxide and benzoin were mixed, and then introduced into a cylindrical glass dilatometer which consists of a reaction vessel, 1.3 cm. in diameter and 15 cm. in length with a capillary tube of 25 cm. After removing the gas dissolved in the solution under reduced pressure and below −50°C, the dilatometer was sealed off and held in a thermostat at 50°C.

The initial concentration of benzoyl peroxide and benzoin was 10^{-2} mol. both per liter. The decrease in volume of the solution was followed by a travelling microscope. As the extent of conversion is directly proportional to the extent of decrease in volume of the solution, the former can be calculated by measuring the latter. In order to find the ratio of the extent of conversion to that of decrease in volume, five dilatometers containing polymerized solution were taken at random and each polymer was dried under reduced pressure and weighed. The mean value of the ratio was found to be 3.63 which is very close to the value, 3.65, reported by Starckweather et al.[4].

The temperature in the dilatometer increases somewhat owing to the inefficient dissipation of the heat of reaction; however, as the increment was at most 0.5°C, the temperature might be taken as constant during the polymerization.

* Presented at the Chugoku-Shikoku Local Meeting of the Chemical Society of Japan, Niihama, October 19 (1956).

1) W. Kern, *Makromol. Chem.*, **1**, 209, 246 (1947); W. Kern, R. Schulz and J. Stallmann, ibid., **6**, 216 (1951); W. Kern and R. Schulz, ibid., **13**, 210 (1954).

2) F. Haber and P. Weiss, *Proc. Roy. Soc. London*, A **147**, 332 (1934).

3) J. Ukida, *Chem. High Polymers* (*Kobunshi Kagaku*), **10**, 358 (1953).

4) H. G. Starckweather and G. B. Taylor, *J. Am. Chem. Soc.*, **52**, 4708(1930).

Results and Discussion

The extent of conversion, y, can be defined as a fraction of monomer converted into polymer, i. e. $1-[M]/[M]_0$, where [M] and $[M]_0$ are the concentrations of the monomer at $t=t$ and $t=0$, respectively. The plots of y against t for various initial concentrations of the ferrous ion, x, in the case of the polymerizations of vinyl acetate containing 20% ethanol are shown in Fig. 1.

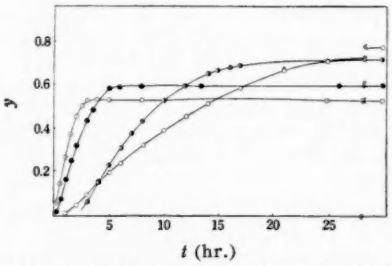

Fig. 1. Polymerization of vinyl acetate in 20% ethanol at 50°C.
$x\cdot10^4$ (mol./l.):
○ 0, ◑ 1.0, ● 5.0, ⊙ 10.0

As seen in Fig. 1, the rate of conversion depends on the amount of ferrous salt added. In the case of rapid polymerization, the increasing viscosity of the solution at high conversion causes distortion of the meniscus and makes accurate reading difficult. Considerably sharp curvatures shown in Fig. 1 would be due to this reason.

TABLE I
DEPENDENCE OF MOLE RATIO AND FERROUS ION CONCENTRATION ON THE INITIAL RATE OF CONVERSION, THE EXTENT OF CONVERSION AND INDUCTION PERIOD

r	$x\cdot10^4$ (mol./l.)	$(dy/dt)_0^2\cdot10^2$ (hr.$^{-2}$)	y_∞	Z	ind. period (hr.)
0.63	0.0	0.14	0.740	0.55	—
	2.5	0.16	0.649	0.91	4.0
	5.0	0.20	0.649	0.91	1.5
	10.0	0.25	0.597	1.20	1.5
1.89	0.0	0.12	0.791	0.41	7.5
	1.0	0.42	0.709	0.66	1.5
	5.0	1.00	0.600	1.18	1.5
	10.0	1.96	0.547	1.61	1.0
2.52	0.0	0.25	0.773	0.45	1.0
	1.0	0.96	0.715	0.63	2.5
	5.0	2.90	0.595	1.23	0.2
	10.0	6.76	0.523	1.82	—
5.67	0.0	0.25	0.825	0.33	1.0
	1.0	0.80	0.792	0.41	—
	5.0	4.00	0.737	0.56	—
	10.0	9.00	0.655	0.94	—

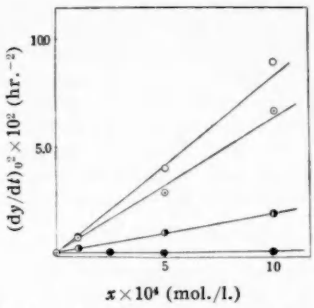

Fig. 2. Dependence of the rate of conversion on x for various values of mole ratio r.
r: ● 0.63, ◑ 1.89, ⊙ 2.52, ○ 5.67

The square of the initial rate of conversion, $(dy/dt)_0^2$, the extent of conversion when no more polymerization proceeds, y_∞, and the value of induction period are listed in Table I. For each value of mole ratio, r, of the initial concentration of the monomer to that of ethanol, the plot of the square of $(dt/dy)_0$ against x, gives a straight line shown in Fig. 2. This relation may be derived kinetically in the following manner.

The polymerization of vinyl acetate is initiated by the radicals produced from the decomposition of benzoyl peroxide. Assuming a stationary state with benzoate radicals, the rate of polymerization can be expressed as follows:

$$-d[M]/dt=(k_p/k_t^{1/2})\times(k_d+k_1[Fe^{2+}])^{1/2}[P]^{1/2}[M] \quad (3)$$

where [M] and $[Fe^{2+}]$ are the concentrations of the monomer and the ferrous ion, respectively, and k_p, k_t and k_d are the rate constants of chain growth, chain termination and apparent spontaneous decomposition of benzoyl peroxide, respectively.

The thermal decomposition of benzoyl peroxide in ethanol is of the first order with respect to the concentration of benzoyl peroxide and the rate of decomposition is the sum of a spontaneous cleavage and a radical induced chain reaction[5]. The following expression for the ferrous ion concentration may be derived from reactions 1 and 2:

$$k_1[P][Fe^{2+}]=2k_2[BzH_2][Fe^{3+}] \quad (4)$$

5) S. Kato and F. Mashio, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kôgyô Kagaku Zassi*), **59**, 380 (1956).

The rate of reaction 2 may be appreciably slower than that of 1[3], therefore, the rate determining step of this redox system may be involved in 2. As mentioned above, the initial concentrations of benzoyl peroxide and benzoin have been chosen as the same and they are much greater than that of the ferrous ion. In this case, the ferrous-ion concentration can be expressed as

$$[Fe^{2+}] = (2k_2/k_1)x \qquad (5)$$

Therefore, the concentration of ferrous ion in the polymerizing solution may be directly proportional to that of ferrous ion added. From Eqs. 3 and 5, the following expression for the initial rate of conversion can be derived:

$$(dy/dt)_0^2 = (k_p^2/k_t)[P]_0(k_d+2k_2x) \qquad (6)$$

This equation corresponds to the curves in Fig. 2.

The initial rate of polymerization is, however, greatly affected by the mole ratio, r, as shown in Table I. In deriving Eq. 6, ethanol was assumed to be an ideal solvent which would not affect $(dy/dt)_0$; however, if a new radical which is produced from a molecule of ethanol attacked by a growing radical, is not so active as to initiate a new chain, ethanol will act as inhibitor or retarder. However, this reason may be invalidated by the fact that $(dy/dt)_0$ was approximately constant and independent of the ratio, r, in the absence of ferrous ion. The dependence of the rate of conversion on the ratio r, therefore, would be ascribed to the changes of the rate constants k_1 and k_2, which would be affected by the composition of the solution.

From the curves in Fig. 2, the ratio k_2/k_d can be calculated; for example, k_2/k_d is about 12,000 for $r=2.52$, showing that a small amount of ferrous chloride accelerates efficiently the rate of polymerization in this redox system.

The concentration of benzoyl peroxide at time t may be expressed as

$$[P] = [P]_0 \exp\{-(k_d+2k_2x)t\} \qquad (7)$$

in the early stage of polymerization.

Substituting Eq. 7 into Eq. 3, and integrating from $t=0$ to $t=t$, it follows:

$$\ln(1-y) = (2k_p/k_t^{1/2})[P]_0^{1/2}(k_d+2k_2x)^{-1/2} \times [\exp\{-(k_d+2k_2x)t/2\}-1] \qquad (8)$$

The concentration of benzoyl peroxide, however, will be reduced more rapidly than that of benzoin, for the former decomposes not only in the reaction 1, but it will also decompose thermally. The concentration of ferrous ion, therefore, will be increased gradually. But assuming the concentration of ferrous ion to be constant, the extent of conversion at sufficient time of duration, y_∞, can be expressed as:

$$Z \equiv \{1/\ln(1-y_\infty)\}^2 = (k_t/4k_p^2[P]_0)(k_d+2k_2x) \qquad (9)$$

The values of Z are listed in Table I. From Eq. 9, it is expected that a plot of Z against x would give a straight line. Fig. 3 shows the relation between Z and x, and it is seen that the extent of conversion decreases with increasing ferrous ion concentration for each value of r. The abnormal decrease of Z with monomer concentration 90%, may be ascribed to the decrease of k_t due to the increased viscosity at a high conversion[6].

Eq. 9 has been introduced on the assumption that none of the velocity constants nor the ferrous ion concentration vary through the polymerization processes. But, these would actually vary with the change in the composition of the solution. However, it is possible, in principle, to calculate the value of x that makes the extent of conversion at any time t maximum.

If the right-hand side of Eq. 8 is differentiated with respect to x and the result equated to zero, the condition for the minimum of $\ln(1-y)$ and hence the maximum of y may be obtained. The relationship found is

$$\exp(k_d+2k_2x)t/2 = 1+(k_d+2k_2x)t \qquad (10)$$

Two solutions of this equation may be obtained graphically, i.e.,

$$(k_d+k_2x)t/2 = 0 \qquad (11)$$

$$k_d+2k_2x \cong 2.5/t \qquad (12)$$

Since neither k_d nor k_2 is zero, Eq. 11 has no physical meaning. It may be said that Eq. 12 is the relation between x and the time t when the extent of conversion y with the initial ferrous ion concentration x becomes of greater value than any other one.

The rate constants k_d and k_2 can be calculated from Figs. 2 and 3 which correspond to Eqs. 6 and 9, respectively, though it is very doubtful whether each rate constant in Eq. 9 has kept up its original meaning.

The values of k_d and k_2 thus obtained

6) G. V. Schulz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947).

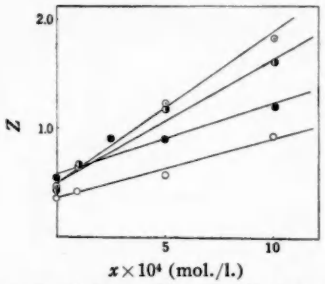

Fig. 3. Relation between Z and x for each value of r.
r: ● 0.63, ◑ 1.89, ⊙ 2.52, ○ 5.67

were 0.07 hr.$^{-1}$ and 300 l. mol.$^{-1}$ hr.$^{-1}$, respectively, and the ratio k_2/k_d was about 4,300 which was much less than that obtained only from Eq. 6. The cause of this discrepancy may be ascribed to the reason mentioned above.

It is of interest, however, to test Eq. 11. Substitution of those numerical values into Eq. 12 leads to Eq. 13, i. e.,

$$0.07+600x\cong2.5/t \qquad (13)$$

For a series of x, the corresponding time was calculated from Eq. 13 and compared with one obtained experimentally from Fig. 1.

It is noted, as seen in Table II, that the values of t calculated are in fairly good agreement with those obtained experimentally.

TABLE II
COMPARISON OF CALCULATED VALUES OF t WITH THOSE OBSERVED

$x\cdot10^4$ (mol. l^{-1})	t (calcd.) (hr.)	t (obsd.) (hr.)
10	4	~ 4
5	7	4~12
1	18	12~25
0	36	25~

Summary

Polymerization of vinyl acetate in the benzoyl peroxide-iron-(II)-benzoin redox-system was studied in ethanol. From the extent of decrease in volume, the rate of conversion was calculated. It was found that the square of the initial rate of conversion was proportional to the initial concentration of ferrous ion and that the extent of conversion at the time when the polymerization was finished, decreased with increasing amount of ferrous ion which was added.

The initial rate of conversion in this redox system was found to depend also on the mole ratio of the monomer to ethanol. The reason might be ascribed to the change in the rate constant.

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Behavior of Zirconium-95 and Niobium-95 in Dilute Hydrochloric Acid toward Cation Exchange Resin

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(Received February 26, 1958)

Zirconium and niobium nuclides contained in fission products are ^{95}Zr—^{95}Nb and ^{97}Zr—^{97}Nb. The abundance of short-lived ^{97}Zr—^{97}Nb becomes negligibly small in a cooling period of about 10 days, while that of comparatively long-lived ^{95}Zr—^{95}Nb increases to the maximum after a longer period of about 200 days. Even after a few years, its abundance is still remarkable[1].

Zirconium-95 and niobium-95 in a mineral acid solution are present as radiocolloids[2] and the chemical behavior of these colloids is very complicated. Although many investigations[3] have been made regarding the chemical separation of ^{95}Nb from ^{95}Zr, the behavior of these nuclides toward the

1) H. F. Hunter and N. E. Ballow, *Nucleonics*, **9**, No. 11, C-2(1951).

2) J. Schubert and E. E. Cohn, ibid., **4**, No. 6, 2 (1949); J. Schubert and J. W. Richter, *J. Colloid Sci.*, **5**, 376 (1949).

3) K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **73**, 2900 (1951); **73**, 9 (1951); R. E. Wacker and W. H. Baldwin, AEC report, *ORNL*, 637 (1950).

cation exchange resin has not been thoroughly investigated. The author has made a study of the difference in the adsorbability of ^{95}Zr and ^{95}Nb to the cation exchange resin and also the effects of conditions of preparing solutions on the adsorbability.

Experimental

Material.—Zirconium-95 was obtained as oxalate complex from U.S.A.E.C.. Since it has been allowed to stand for about one year, ^{95}Zr and its daughter, ^{95}Nb, must be in transient equilibrium. The activity of this material was about 100 μC. To this, 10 ml. of concentrated sulfuric acid was added and heated slowly to almost dryness. After repeating this step twice more, the residue was heated with 200 ml. of 0.2 N hydrochloric acid to be dissolved. An aliquot of this solution, having an activity of about 1 μC, was used as a sample. The aliquot contained about 10^{-13} mole each of ^{95}Zr and ^{95}Nb, thus corresponding to about 5×10^{-11} mol./l., respectively.

Procedures.—After slurring the cation exchange resin Dowex 50-X8 (100 to 200 mesh) was placed in a glass tube, the resin was washed with 3 N hydrochloric acid to convert it into the hydrogen form and further washed completely with demineralized water. After complete washing, the interstitial water was replaced by 0.2 N hydrochloric acid. The resin bed was 0.7 cm. in diameter, 6.5 cm. in length and its volume was 2.5 ml.. A 2 ml. aliquot of the 0.2 N hydrochloric acid solution of ^{95}Zr—^{95}Nb mixture was diluted to 20 ml. with 0.2 N hydrochloric acid and poured into the column. Then 70 ml. of 0.2 N hydrochloric acid, 20 ml. of demineralized water, and 40 ml. of 0.5% oxalic acid solution or 3 N hydrochloric acid were poured successively. The flow rate was 0.5 ml. per minute. The 2 ml. fractions of the effluent were poured successively into the glass dishes which were 2.5 cm. in diameter and 0.6 cm. in height, and then heated with an infrared lamp to dryness. The activity in the dishes was measured by a G.M. counter whose window was 2.5 mg./cm^2 in thickness. The distance between the test sample and the window was 1.5 cm. and about 8% of the total activily was counted.

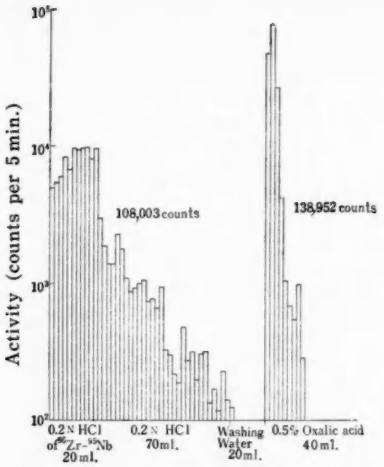


Fig. 1. Elution of a ^{95}Zr—^{95}Nb mixture. effluent fraction: 2 ml.

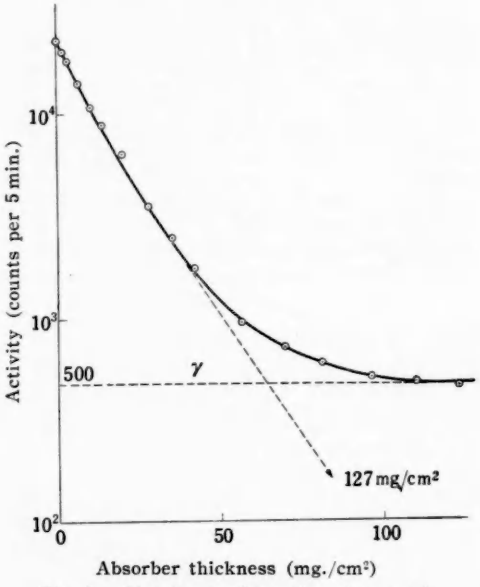


Fig. 2. Aluminum absorption curve of 0.5% oxalic acid fraction.

Results

Difference in Adsorbability of ^{95}Zr and ^{95}Nb.—The results obtained by the above mentioned procedures are shown in Fig. 1. It will be seen that ^{95}Zr—^{95}Nb mixture could be separated into two fractions; the one eluted by 0.2 N hydrochloric acid and the other by 0.5% oxalic acid. To identify ^{95}Zr and ^{95}Nb in these fractions, the maximum β-energy of the fraction activity was determined using a set of aluminum abosorbers. Instead of measuring the maximum β-energy of activities on all dishes, suitable aliquots of two fractions of 0.2 N hydrochloric acid and 0.5% oxalic acid were evaporated to dryness and the β-energy was measured. The results are shown in Figs. 2 and 3. The values of maximum range in Figs. 2 and 3, converted into MeV., agree with those for ^{95}Zr—β and ^{95}Nb—β in Table I. As shown

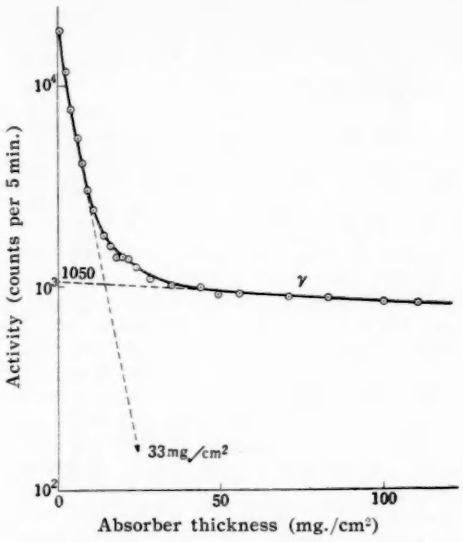


Fig. 3. Aluminum absorption curve of 0.2 N HCl fraction.

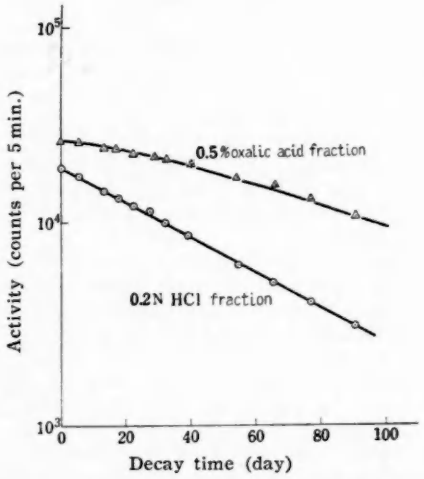


Fig. 4. Decay curves of two fractions.

TABLE I.

Nuclide	Half-life (day)	λ(day^{-1})	β(MeV)	γ(MeV)
^{95}Zr	65	0.01066	0.364	0.754
^{95}Nb	35	0.0198	0.165	0.76

in Fig. 4, the decay curve of the 0.5% oxalic acid fraction shows the production of ^{95}Nb from ^{95}Zr. After 26 days, the curve shows a half-life of 65 days. On the other hand, the activity of the 0.2 N hydrochloric acid fraction decayed with a half-life of 35 days. These half-life values coincide with those of ^{95}Zr and ^{95}Nb shown in Table I.

From the measurement of the maximum β-energy and the half-life, it was found that the 0.2 N hydrochloric-acid fraction contained mainly ^{95}Nb and the 0.5% oxalic-acid fraction mainly ^{95}Zr.

Relation between Time of Preserving the Solution of ^{95}Zr—^{95}Nb and the Adsorbability of ^{95}Zr.—Since ^{95}Zr and ^{95}Nb in a mineral acid solution are present as radiocolloids, it was thought probable that there might be an appreciable difference in adsorbability toward a cation exchanger between a fresh solution and an aged solution of ^{95}Zr—^{95}Nb.

After storage of the fresh sample solutions which were prepared as described before for 3, 7, 10 and 15 days, the experiments were carried out similarly. The results are shown in Fig. 5. It is obvious

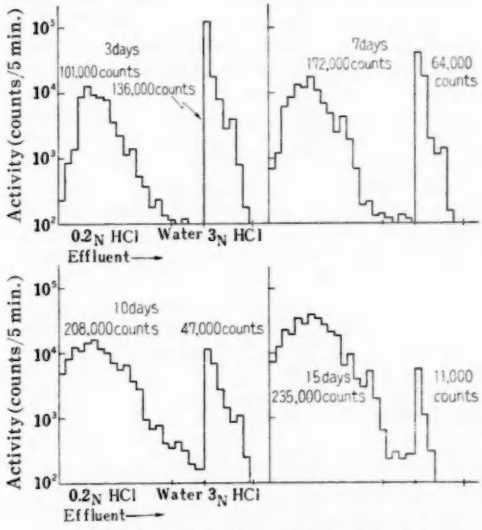


Fig. 5. Time of keeping solution of ^{95}Zr and ^{95}Nb and adsorbability of ^{95}Zr.

that the amount of ^{95}Zr retained on the resinbed decreases as time passes. when thesolution is 10 days old, ^{95}Nb and a considerable amount of ^{95}Zr are eluted in the same fraction. This phenomenon may be related to the characteristics of ^{95}Zr, the pH, other ions and dust in the solution, the wall of the vessel, etc., but can not be defined quantitatively.

Variation in Adsorbability of ^{95}Zr and ^{95}Nb with the Concentration of Hydrochloric Acid.—Two fractions of ^{95}Zr and

^{95}Nb were obtained by the procedure described above, and each fraction was converted into 0.2 N hydrochloric acid solution. To 0.1 ml. aliquots of these solutions 25 ml. of hydrochloric acid having the following concentrations was added respectively: 0.01, 0.02, 0.04, 0.06, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 1.0, 1.9, 2.85 and 3.8 N. The addition of the small volumes of ^{95}Zr or ^{95}Nb solution did not appreciably change the hydrochloric acid concentrations of the resultant solutions. The activities of ^{95}Zr or ^{95}Nb in these solutions were about 0.5 μC corresponding to 10^{-13} mole (5×10^{-12} mol./l.).

These solutions were transferred to glass-stoppered flasks containing one gram each of air-dried Dowex 50—X8 (100 to 200 mesh) which had been treated with hydrochloric acid, and were agitated for five hours, at 25°C. Five-hour agitation was sufficient to give constant adsorption values. After the resin had settled the aliquots of the supernatant solution were transferred to glass dishes, evaporated to dryness, and their activities were measured. Also the entire procedure was run without the addition of the resin. Fig. 6 shows the relation between the adsorbability (%) of ^{95}Zr and ^{95}Nb and the concentration of hydrochloric acid. The adsorbability is defined by the ratio of the difference in activity between the aliquot obtained without resin and that with resin to the activity of the aliquot obtained without resin.

Fig. 6 indicates that about 0.2 N hydrochloric acid is suitable for the separation of ^{95}Zr from ^{95}Nb. As mentioned already,

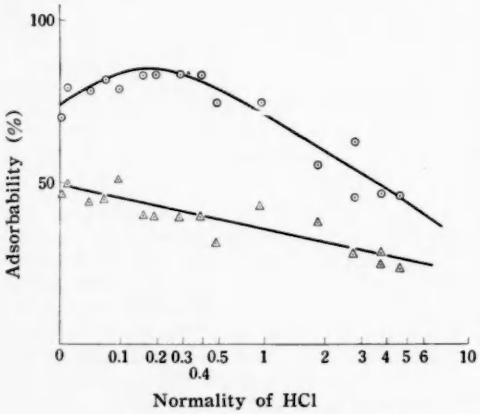


Fig. 6. Effect of hydrochloric-acid concentration on the absorbability of ^{95}Zr and ^{95}Nb.

the adsorption of neither nuclide is due to the ion exchange. Consequently the complete separation of ^{95}Zr from ^{95}Nb is difficult even though there is a difference in adsorbability of both nuclides. Nevertheless by repeating the procedures a complete separation will be possible. It is also indicated that 3 N hydrochloric acid may be used as an eluent for ^{95}Zr instead of 0.5% oxalic acid. This was later confirmed experimentally.

Effect of Concentrations of Zr and Nb. —It was thought desirable to investigate the separation of larger amounts of ^{95}Zr and ^{95}Nb than 0.5 μC. Because of the limited amounts of these nuclides, non-active isotopes were used as carriers. For this purpose a solution of reagent grade zirconium oxychloride ($ZrOCl_2\cdot8H_2O$) and an oxalic acid solution of niobium pentoxide previously fused with potassium bisulfate were prepared. From these solutions, four solutions containing 10^{-9}, 10^{-8}, 10^{-7}, and 10^{-6} mol./l. each of zirconium and niobium were prepared, and 10^{-13} mol./l. each of ^{95}Zr and ^{95}Nb was added as tracers. These four solutions were then treated with concentrated sulfuric acid, and processed as mentioned above. As a result, in all the cases tested, the degree of separation of ^{95}Nb from ^{95}Zr was the same as that with 0.5×10^{-11} mol./l. It may be concluded that the separation of ^{95}Nb from ^{95}Zr is possible under the conditions described in the experimental part, in the concentration range 10^{-12} to 10^{-6} mol./l.

Effect of Strontium. — Schubert[2] reported that the state of tracer amounts of ^{95}Zr and ^{95}Nb in dilute mineral acid was radiocolloid and the adsorbability of these nuclides to a cation exchanger increased with the concentration of other cations. In the group-separation of fission products with a cation exchange resin, it is often the case that the complicated behavior of ^{95}Zr—^{95}Nb makes their complete separation impossible[4,5]. As a large amount of strontium is found in fission products, the effect of this ion on the adsorbability of ^{95}Zr and ^{95}Nb was investigated to solve this problem. The sample solution contained about 2 μC of ^{95}Zr—^{95}Nb (about 10^{-12} mol.) in a volume

4) E. R. Tompkins, J. X. Khym and W. E. Chon, *J. Am. Chem. Soc.*, **69**, 2769 (1947); W. E. Cohn, G. W. Parker and E. R. Tompkins; *Nucleonics*, **3**, No. 5, 22 (1948).

5) T. Shiokawa, T. Ozaki, T. Kambara and M. Yagi, *The 1st Atomic Energy Symposium*. (1957), Tokyo, Japan, Section: Material and Chemistry, B-33.

of 20 ml. of 0.2 N hydrochloric acid. To a series of this solution, 1 mg. (0.571×10^{-3} mol./l.), 2 mg. (1.141×10^{-3} mol./l.), 3 mg. (1.712×10^{-3} mol./l.), and 4 mg. (2.282×10^{-3} mol./l.) of strontium (as chloride) were added respectively. After passing 20 ml. of the sample solution through the same resin column as described before, elution was done successively with 50 ml. of 0.2 N hydrochloric acid, 30 ml. of washing water, and 50 ml. of 3 N hydrochloric acid. The results are shown in Figs. 7, 8, 9 and 10. It is pointed out that, when the strontium concentration is 2.282×10^{-3} mol./l., ^{95}Nb is eluted with difficulty with 0.2 N hydrochloric acid (Fig. 10). In other words, separation of ^{95}Nb from ^{95}Zr becomes impossible under such a condition.

In the group separation of ^{95}Zr and ^{95}Nb from fission products using a cation exchange resin, a good recovery may be obtained when 0.2 N hydrochloric acid

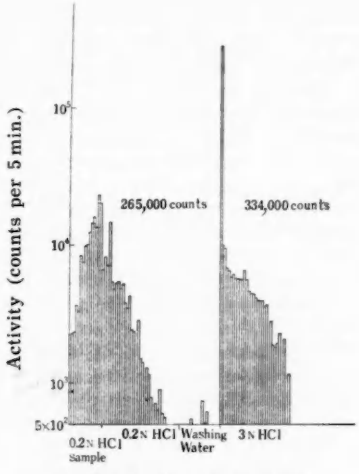


Fig. 7. Effect of 1 mg. Sr^{2+}. Sample solution: 20 ml.

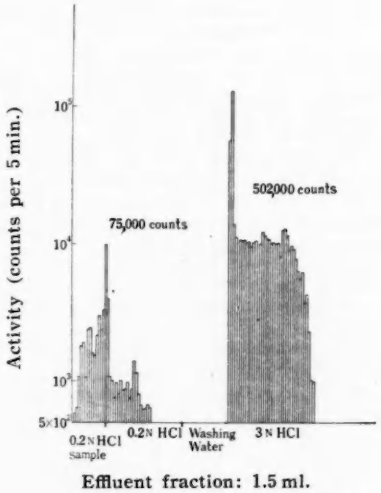


Fig. 8. Effect of 2 mg. Sr^{2+}. Sample solution: 20 ml.

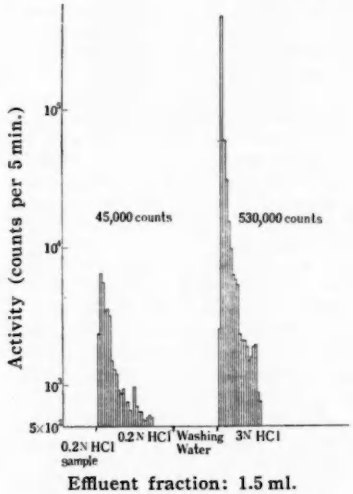


Fig. 9. Effect of 3 mg. Sr^{2+}. Sample solution: 20 ml.

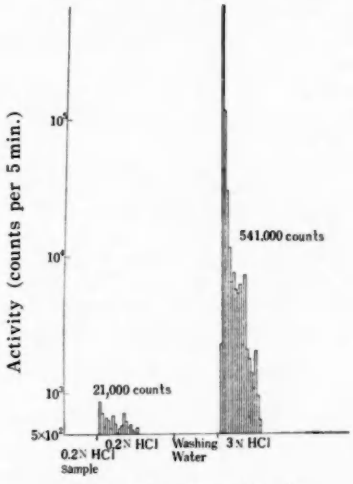
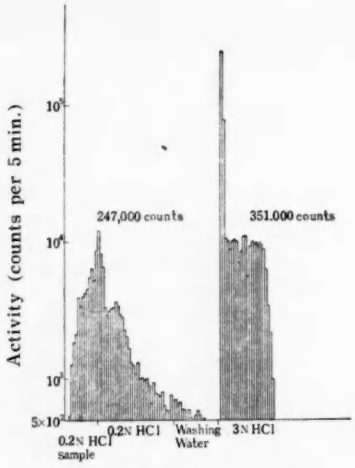


Fig. 10. Effect of 4 mg. Sr^{2+}. Sample solution: 20 ml.



Effluent fraction: 1.5 ml.

Fig. 11. Effect of 2 mg. Sr^{2+} previously adsorbed.

solution of ^{95}Zr and ^{95}Nb containing a large amount of strontium is passed through the resin and the elution of two nuclides is made with 0.5% oxalic acid.

When 2 mg. of strontium was first adsorbed to the resin column and then a solution of ^{95}Zr—^{95}Nb was poured into the column, the result shown in Fig. 11 was obtained. By comparing Fig. 8 with Fig. 11, it is seen that the activity of ^{95}Nb in the effluent is greater in the latter. It is believed that this is due to the change in the state of ^{95}Nb rather than to the variation of the resin surface. The effect of the cations other than the strontium ion will be studied in future.

Separation of ^{95}Zr and ^{95}Nb Using Other Cation Exchangers.—According to Schallert[6], ^{95}Zr and ^{95}Nb were strongly adsorbed by Amberlite IR-1 and IR-100. As these resins were no more available, experiments were carried out with Amberlite IR-120 and Diaion SK. The results were the same as those with Dowex 50-X8.

Adsorption of ^{95}Zr and ^{95}Nb to a Glass Vessel.—It is said that the tracer amounts of ^{95}Zr and ^{95}Nb in dilute mineral acid were adsorbed on a glass vessel[7]. In the present work, a solution of ^{95}Zr that had been kept in a soft-glass bottle for 30 days did not show any appreciable loss due to the adsorption. On the other hand, about 0.5% of ^{95}Nb activity was lost when 0.2 N hydrochloric acid solution of ^{95}Nb had been kept in a glass bottle for 3 days, and considerable activity was lost when this solution had been kept for 30 days.

6) P. O. Schallert, AEC report, *ORNL*-1144, (1952).

Summary

By passing 0.2 N hydrochloric acid solution of tracer amounts of ^{95}Zr and ^{95}Nb (about 10^{-11} mol./l., 10^{-13} mol., or 1 μC, with respect to each nuclide) through a cation exchange resin column (Dowex 50—X8, Amberlite IR-120, or Diaion SK) and eluting with 0.2 N hydrochloric acid, a fraction containing mainly ^{95}Nb was obtained. A fraction containing mainly ^{95}Zr was then obtained by eluting with 0.5% oxalic acid or 3 N hydrochloric acid. With higher concentrations of non-active zirconium and niobium (about 10^{-6} mol./l. each), similar results were also obtained.

As the 0.2 N hydrochloric acid solution of ^{95}Zr—^{95}Nb became aged, the adsorbability of ^{95}Zr decreased. Effect of hydrochloric acid concentration on the adsorbability of ^{95}Zr and ^{95}Nb was studied and the concentration range 0.1 to 0.3 N was found to be suitable for separation.

The adsorbability of ^{95}Nb increased with an increase in the concentration of strontium ion.

This work has been done in the laboratories of the Government Chemical Industrial Research Institute, Tokyo. The author wishes to express his thanks to Dr. Toshio Nakai for helpful suggestions and guidance in the course of this work. Thanks are also due to Dr. Kenjiro Kimura for his advice and encouragement. The helpful suggestions of Mr. Hiroshi Onishi in the preparation of this manuscript are also acknowledged.

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7) A. G. Maddock and W. Pugh, *J. Inorganic and Nuclear Chem.*, **2**, 144 (1956).

Investigation on Dissolving Pulp. XIV. Some Behavior of Wood Pulp and Cotton Linters in Phosphoric Acid

By Tokumi KOSHIZAWA

(Received march 19, 1958)

In a previous paper[1], the author investigated the solubility of various kinds of cellulose into phosphoric acid to know the details of mechanism of the phosphoric-acid swelling which was observed in Heide's test for cellulose reactivity[2], and pointed out the influence of other factors than the degree of polymerization as shown by a Ekenstam[3] on the solubility of various kinds of cellulose into phosphoric acid.

In this paper, the dissolved part of cellulose (sulfite pulp, prehydrolyzed sulfate pulp and cotton linters) in phosphoric acid of various concentrations was studied with regard to the average degree of polymerization, and the rates of hydrolysis in 70% phosphoric acid at 20°C. The rates of hydrolysis of the insoluble residues, swelled to various degrees were also determined.

Experimental

1) Solubility of Cellulose into Phosphoric Acid and Average Degree of Polymerization of Dissolved Part.—First cellulose samples were pretreated with 73.3% phosphoric acid for 10 min. at 20°C, then the proper amount of 82, 86 or 90% phosphoric acid was added drop by drop to get the required concentration under costant stirring, at the constant temperature, 20°C. After 20 minutes, 58% phosphoric acid was added to dilute the solution to 70% Ten minutes after the dilution, the solution was centrifuged and the supernatants were filtered through a glass filter (1G-3). The filtrate was diluted properly and its viscosity was determined in Ostwald's viscometer. The change of viscosity with time in 70% phosphoric acid at 20°C was plotted and the extrapolated value of viscosity to time 0 was determined graphically. Intrinsic viscosity $[\eta]$ was determined by the usual method to plot η_r against various concentrations of the solute. The solubility of cellulose was determined by the oxidation with potassium bichromate and iodometry.

2) The Average Degree of Polymerization of Insoluble Residue.—Insoluble residue in 1 was poured into a large quantity of ice-cold water, washed repeatedly with distilled water, and dried. The cellulose residue was dissolved into cupro-ammonium solution and its viscosity was determined to know the average degree of polymerization. The sample was also dissolved into 85% or 90% phosphoric acid after pretreatment with 73.3% phosphoric acid. After complete dissolution—it takes about 30~60 min.—, to the solution was added 58% phosphoric acid until the concentration of the solution became 70% and the intrinsic viscosity in 70% phosphoric acid was determined by the extrapolation of the viscosity curves to the zero time. The constant K_m of cellulose in 70% phosphoric acid was calculated from the $[\eta]$ and the K_m constant (5×10^{-4}) in cupro-ammonium solution, and $[\eta]$ in the phosphoric acid solution. The value in 70% phosphoric acid thus obtained is about 13×10^{-4}. But this value is not exact and serves only to know the relative change of DP.

Results and Discussion

(1) Average Degree of Polymerization of Dissolved Part.—The solubility curves of sulfite pulp, prehydrolyzed sulphate pulp, and cotton linters were shown in Fig. 1. The average degrees of polymerization of cellulose dissolved into the acid of various concentrations were shown in

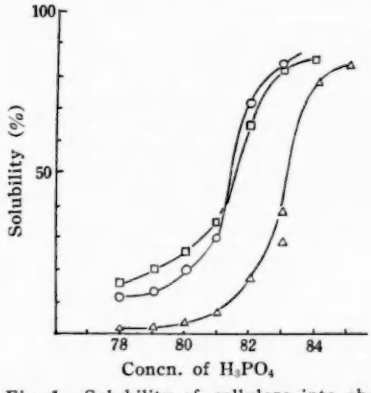


Fig. 1. Solubility of cellulose into phosphoric acid.
△: Cotton linters, ○: Sulfite pulp,
□: Prehydrolyzed sulfate pulp

1) T. Koshizawa, *J. Soc. Textile and Cellulose Ind., Japan (Sen-i Gakkaishi)*, in press (Part XII of this paper).
2) K. Heid, *Faserforsch. u. Textil Techn.*, **3**, 486 (1952).
3) Alf af Ekenstam, *Svensk papperstidn*, **45**, 81 (1942).

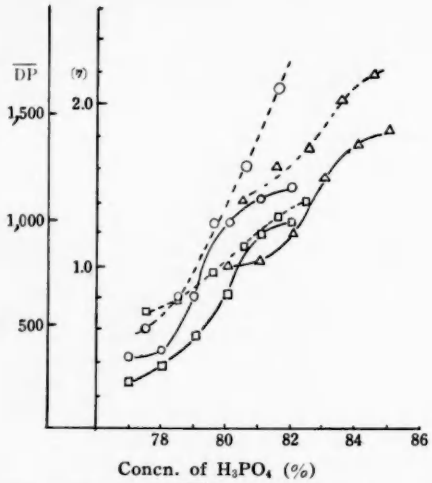


Fig. 2. [η] and $\overline{DP}$ of dissolved part.
△: Cotton linters, ○: Sulfite pulp,
□: prehydrolyzed sulfate pulp.
——: [η] and $\overline{DP}$ of dissolved part,
----: [η] and $\overline{DP}$ of dissolved part corresponding to 1% increase in phosphoric acid concn.

Fig. 2. The degree of polymerization was calculated from [η] using the K_m 13×10^{-4}. Although the K_m constant derived from the comparison of [η] in cupro-ammonium solution and [η] in phosphoric acid solution might not be an exact value, it would be sufficient to discuss the relative difference, as in the present case. The dotted lines in Fig. 2 are the average degree of polymerization of the dissolved part corresponding to the increase in the concentration of phosphoric acid by 1%. The values were calculated from the curves in Fig. 1 and unbroken lines in Fig. 2. In the calculation the assumption that the viscosity shows the weight average of degree of polymerization was taken. The degree of polymerization of newly dissolved part corresponding to the increase in phosphoric acid concentration by a% is calculated from the following relationship,

$$P_{c+a}\times W_{c+a}=P_c\times W_c+P_a\times W_a$$

or $$P_a=(P_{c+a}\times W_{c+a}-P_c\times W_c)/W_a$$

where W_c, W_{c+a} and W_a are weight % of dissolved parts in c%, $c+a$% and a% phosphoric acid, and P_c, P_{c+a} and P_a are their average DP, respectively. Although the above stated assumption might not be strictly valid as we have to consider the distribution of molecular weight or other factors, the curves show us the approximate trends. As seen in the dotted lines in Fig. 2 the average DP of newly dissolved pulp which correspond to the increase in the concentration of phosphoric acid, clearly differ according to the kind of cellulose sample. Namely the increase in concentration of phosphoric acid accompanies a marked increase in the DP of dissolved part in sulfite pulp, while it accompanies a slight increase in the DP in the case of prehydrolyzed sulfate pulp and cotton linters. So the abrupt increase in solubility at a certain concentration of phosphoric acid as shown in Fig. 1 cannot be ascribed solely to the factor of DP as stated by af Ekenstam[3] and suggests the influence of a fine structure such as lateral order upon the solubility of cellulose into phosphoric acid. Needless to say the increase in DP proportional to the increase in concentration of the acid shows the effect of DP, and a relatively large increase in DP with the increase in acid concentration in the case of sulfite pulp may be caused by the wide spread of distribution of DP. The existence of molecules with small DP among large molecules gives much influence upon the solubility or swellability and the fact may be correlated to the lowering of swellability or the hornification caused by cold alkali treatment.

(2) Decrease in Degree of Polymerization in Dissolved and Insoluble Part. —The change of 1/DP of the dissolved part with the time of hydrolysis is shown

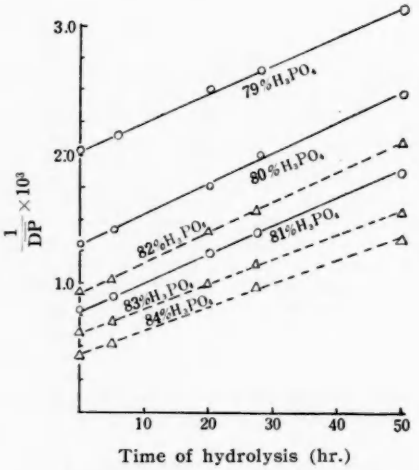
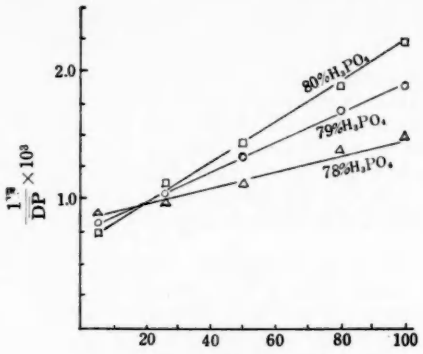
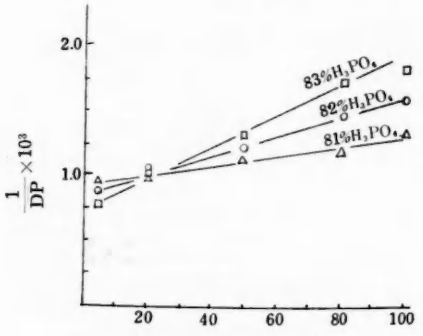


Fig. 3. Degradation of dissolved part in 70% H_3PO_4 at 20°C.
△: Cotton linters, ○: Sulfite pulp.



Time of hydrolysis (hr.)

Fig. 4-1. Degradation of insoluble residue in 70% H_3PO_4 at 20°C. (Sulfite pulp)



Time of hydrolysis (hr.)

Fig. 4-2. Degradation of insoluble residue in 70% H_3PO_4 at 20°C. (Cotton linters)

in Fig. 3 in which the DP is calculated from $[\eta]$ in 70% phosphoric acid, assuming the constant, K_m 13×10^{-4}. Figs. 4-1, and 4-2 shows that of insoluble residues. The rate constant for the hydrolysis can be derived from the following equation

$$K=1/t\,\frac{(1-1/DP_0)}{(1-1/DP_t)}$$

where DP_0 and DP_t are the average DP of the cellulose at zero time and time t, respectively. Expansion of the right side of the equation to an infinite series and neglect of all of the terms other than the first gives the following equation,

$$K=1/t(1/DP_t-1/DP_0)$$

Many investigations[4,5] found the validity of this equation in the initial stage of hydrolysis. The tangents of the curves in Figs. 3 and 4 correspond to the rate

4) O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).
5) Alf af Ekenstam, *Ber.*, **69B**, 549 (1936).

TABLE I

RATE CONSTANT OF HYDROLYSIS OF DISSOLVED PART IN 70% PHOSPHORIC ACID AT 20°C

	Cotton linters	
Concn. of H_3PO_4	82%	$K=3.8\times10^{-7}\,min^{-1}$
	83%	$K=3.0\times10^{-7}\,min^{-1}$
	84%	$K=3.2\times10^{-7}\,min^{-1}$
	Sulfite pulp	
Concn. of H_3PO_4	79%	$K=4.0\times10^{-7}\,min^{-1}$
	80%	$K=4.0\times10^{-7}\,min^{-1}$
	81%	$K=4.0\times10^{-7}\,min^{-1}$

TABLE II

RATE CONSTANT OF HYDROLYSIS OF INSOLUBLE RESIDUE IN 70% PHOSPHORIC ACID AT 20°C

	Cotton linters	
Concn. of H_3PO_4	81%	$K=0.56\times10^{-7}\,min^{-1}$
	82%	$K=1.3\times10^{-7}\,min^{-1}$
	83%	$K=1.7\times10^{-7}\,min^{-1}$
	Sulfite pulp	
Concn. of H_3PO_4	78%	$K=0.85\times10^{-7}\,min^{-1}$
	79%	$K=1.5\times10^{-7}\,min^{-1}$
	80%	$K=2.5\times10^{-7}\,min^{-1}$

constants of hydrolysis which are given in Tables I and II. The rate constant of hydrolysis of dissolved part does not vary in either case of linters or sulfite pulp. On the other hand that of insoluble residue changes with the concentration of phosphoric acid before the dilution to 70%. Namely the rate of hydrolysis depends on the degree of swelling in the solution. Thus we may conclude that the rate of inhomogeneous degradation of cellulose is greatly influenced by the state of molecular orientation. This fact also makes easy the test on swellability of cellulose in phosphoric acid which is proposed by Heide[1] or the test modified by us[1] to determine the transparency or turbidity of the cellulose suspension in phosphoric acid because, on the one hand, the swelled part dissolves into the solution with the lapse of time because of the greater rate of hydrolysis, and, on the other hand, the insoluble residue such as the constricted part in balloon-like swelling remains unchanged, even after a long time because of the lower rate of hydrolysis.

Summary

The average DP of cellulose dissolved into phosphoric acid of various concentrations has been determined by viscometry. The relations of average DP of dissolved

part to the concentration of phosphoric acid are not the same in the three samples —dissolving sulfite pulp, prehydrolyzed sulfate pulp and cotton linters. The fact may be ascribed to the factors such as lateral order other than the degree of polymerization.

The rate of hydrolysis of cellulose in 70% phosphoric acid at 20°C was also determined as to both cases of dissolved part and insoluble residue. The rate of hydrolysis of the dissolved part is almost independent of the kind of cellulose, while that of the insoluble residue greatly depends on the degree of swelling in the solution.

The author wishes to express his hearty thanks to Professor Hiroshi Sobue, Faculty of Engineering, University of Tokyo, for his kind directions. The author also thanks Mr. Toshio Ōba, Kokoku Rayon and Pulp Co. Ltd., for his kind co-operation throughout this work.

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Effect of Substitution on Dipole Moments of Molecules

By Hayami YONEDA

(Received October 26, 1957)

When hydrogen in a molecule RH is replaced by a substituent X, the polarities of the RH and RX bonds will generally differ. Therefore R in RX will be either more positive or more negative than R in RH. This polarity effect is called the inductive effect. Substituents which induce a negative charge on an adjacent atom when they replace hydrogen, are called anionoid inductive (or −I) substituents, and those which induce a positive charge, cationoid inductive (or +I) substituents. Alkyls belong to the former group, and amino, hydroxyl and halogens to the latter group. Thus, when substituents including hydrogen are arranged in the order of +I effect we obtain a series; halogens> hydroxyl> amino> hydrogen> alkyls. Although the inductive effect was postulated by organic chemists in order to understand various chemical properties of organic compounds (e.g. acid strength), still it should be supported by the experimental data of dipole moments. In fact, measurements of dipole moments have confirmed in many cases the existence and the sign of the electron displacement which organic chemists had postulated. For example, the dipole moments of a series of hydrogen halides and the dipole moments of a series of alkyl halides have the same tendency of variation of dipole moments from chloride to iodide; hydrogen chloride > hydrogen bromide > hydrogen iodide and methyl chloride> methyl bromide> methyl iodide. The similar tendency is observed between the two series, methyl chloride> methyl alcohol> methylamine and ethyl chloride> ethyl alcohol> ethylamine.

However, when we examine the data of dipole moments more carefully, we will find out several series of compounds which make us doubt the existence of the definite inductive effect. For example, in a series of water, methyl alcohol and dimethyl ether, the dipole moment should increase in the order water, methyl alcohol and dimethyl ether, as methyl is a −I substituent. The actual order is, however, quite reverse. The purpose of this paper is to find out such anomalous series of compounds which apparently seem to contradict the inductive effect and to establish a general rule which holds good in every case.

Discussion

Data of dipole moments which form the basis of discussion in the present paper are listed in Table I. First, we will consider the series of alkyl halides whose observed dipole moments suggest the existence of the definite inductive effect. From Table I it is easily seen that except in the case of fluorides, the dipole moment increases in the order hydrogen halide,

methyl halide, ethyl halide, etc. and reaches fairly rapidly a definite value in all series of chlorides, bromides and iodides. This tendency can be easily explained when we consider the inductive effect. If hydrogen in methyl is replaced by another methyl, the second methyl induces a negative charge on the carbon of the original methyl and lowers its electron affinity and hence increases its $-I$ activity. Therefore ethyl should be a more active $-I$ group than methyl. Similarly *n*-propyl should be a more active $-I$ group than ethyl, and *n*-butyl should be a more active $-I$ group than *n*-propyl and so on. This second order relayed inductive effect dies away, however, down the chain. Therefore the polarity of the RX bond will be expected to increase from methyl halide to ethyl halide, from ethyl halide to propyl halide, etc. and to reach a certain definite limit. Since the polarity of alkyl itself can be neglected, the bond polarity of the RX bond corresponds directly to the observed dipole moment. Thus the data of dipole moments can be understood simply by the concept of the inductive effect.

TABLE I

DIPOLE MOMENTS* (in Debye unit)

Alcohols		**Bromides**	
H_2O	1.85[1]	HBr	0.79[9]
CH_3OH	1.69[2]	CH_3Br	1.79[11]
CH_3CH_2OH	1.67[2]	CH_3CH_2Br	2.01[11]
$CH_3CH_2CH_2OH$	1.657[3]	$CH_3CH_2CH_2Br$	2.15[11]
$CH_3CH_2CH_2CH_2OH$	1.63[2]	$CH_3CH_2CH_2CH_2Br$	2.15[11]
Ethers		**Iodides**	
CH_3OCH_3	1.29[4]	HI	0.38[8]
$CH_3CH_2OCH_2CH_3$	1.17[4]	CH_3I	1.64[11]
$CH_3CH_2CH_2OCH_2CH_2CH_3$	1.18[4]	CH_3CH_2I	1.87[11]
Sulfur Compounds		$CH_3CH_2CH_2I$	2.01[11]
H_2S	1.1[5]	$CH_3CH_2CH_2CH_2I$	2.08[11]
CH_3CH_2SH	1.39[5]	**Amines**	
CH_3SCH_3	1.40[5]	NH_3	1.466[12]
$CH_3CH_2SCH_2CH_3$	1.58[5]	CH_3NH_2	1.32[4]
Fluorides		$(CH_3)_2NH$	1.02[13]
HF	1.91[6]	$(CH_3)_3N$	0.65[4]
CH_3F	1.808[7]	$CH_3CH_2NH_2$	0.99[13]
CH_3CH_2F	1.92[7]	$(CH_3CH_2)_2NH$	0.90[13]
Chlorides		$(CH_3CH_2)_3N$	0.82[13]
HCl	1.034[8]	**Phosphorus Compounds**	
CH_3Cl	1.83[9]	PH_3	0.55[14]
CH_3CH_2Cl	1.98[10]	$CH_3CH_2PH_2$	1.17[14]
$CH_3CH_2CH_2Cl$	2.04[9]	$(CH_3CH_2)_2PH$	1.4[14]
$CH_3CH_2CH_2CH_2Cl$	2.11[9]	$(CH_3CH_2)_3P$	1.45[14]

* Except for sulfur and phosphorus compounds, all the data were obtained for the vapor state.

1) L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1935**, 971.
2) M. Kubo, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **27**, 65 (1935).
3) J. B. Miles, Jr., *Phys. Rev.*, **34**, 964 (1929).
4) L.G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 1779.
5) Clark, "The Fine Structure of Matter", Vol. II, Part II, "Molecular Polarisation", John Wiley & Sons, Inc., New York, (1938), p. 405.
6) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 171 (1946).
7) C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).
8) C. T. Zahn, *Phys. Rev.*, **24**, 400 (1924).
9) P. C. Mahanti, *Phil. Mag.*, (7) **20**, 274 (1935).
10) K. Higasi, "Bunshi-kozoron no Kiso", "Table of Dipole Moments", Kawade-shobo, Tokyo, (1952), p. 172.
11) L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 158.
12) J. M. A. de Bruyne and C. P. Smyth, *J. Am. Chem. Soc.*, **57**, 1203 (1935).
13) P. N. Ghosh and T. P. Chatterjee, *Phys. Rev.*, **37**, 427 (1931).
14) J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds", Chap. 3, Reinhold Publishing Corporation, New York, (1956), p.129.

As the order of the inductive activities of substituents must be constant in every series of compounds, a similar situation should be expected also in the case of a series of alcohols. That is, it is expected that the dipole moment increases in the order water, methyl alcohol, ethyl alcohol, etc. But this is not the case. As is seen in Table I, the dipole moment decreases in the order water, methyl alcohol, ethyl alcohol, etc. A similar anomaly is also seen in a series of amines. The dipole moment decreases in the order ammonia, methylamine, ethylamine, etc. These two cases are related with variation of dipole moments which is caused by the second-order inductive effect. If such an anomaly is not caused by chance but comes from the definite origin, it can be expected to be seen more clearly in cases where the first-order inductive effect is related, because the first-order effect is stronger than the second-order one. Indeed this expectation is realized. As is seen in Fig. 1 the dipole moment decreases stepwise when hydrogen atoms of water and ammonia are replaced successively by alkyl groups.

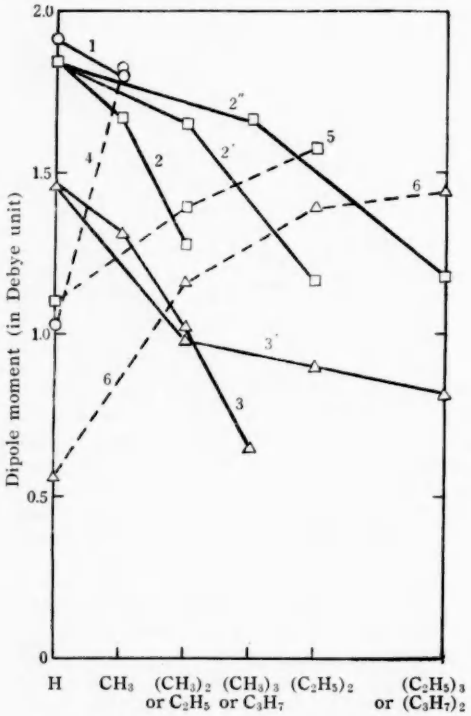

Fig. 1. Variation of dipole moments of various hydrides with successive alkyl substitution.

1 -○—○- HF and CH_3F
2 -□—□- H_2O, CH_3OH and $(CH_3)_2O$
2' -□—□- H_2O, C_2H_5OH and $(C_2H_5)_2O$
2'' -□—□- H_2O, C_3H_7OH and $(C_3H_7)_2O$
3 -△—△- NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$
3' -△—△- NH_3, $C_2H_5NH_2$, $(C_2H_5)_2NH$ and $(C_2H_5)_3N$
4 -○—○- HCl and CH_3Cl
5 -□—□- H_2S, C_2H_5SH and $(C_2H_5)_2S$
6 -△—△- PH_3, $C_2H_5PH_2$, $(C_2H_5)_2PH$ and $(C_2H_5)_3P$

In Fig. 1 the variations of dipole moments of a series of hydrogen sulfide, ethyl mercaptan, diethyl sulfide and of a series of phosphine, ethyl phosphine, diethyl phosphine, triethyl phosphine are also plotted. Both series indicate the existence of the normal inductive effect. In Fig. 1 the dipole moments of hydrogen fluoride, methyl fluoride and hydrogen chloride, methyl chloride are also plotted. The variation of the dipole moment from hydrogen chloride to methyl chloride is normal, while the variation of the dipole moment from hydrogen fluoride to methyl fluoride is abnormal. Here it must be noticed that such an anomaly appears only in hydrogen fluoride, water, ammonia and their alkyl derivatives. That is, the anomaly appears only in the hydrides and their alkyl derivatives of elements in the second period in the periodic table. Here it must be stated that such an anomaly was not discovered suddenly by the present author, but that its discovery was due to the works of Sidgwick[15] and of Parry[16]. Sidgwick suggested a very interesting empirical rule about the coordinating ability of various donor groups. In the series of alkyl derivatives of water and ammonia, the affinity of a donor group toward a metal ion decreases rapidly in the order water, methyl alcohol, dimethyl ether and ammonia, methylamine, dimethylamine and trimethylamine, while in a series of alkyl derivatives of hydrogen sulfide the affinity toward a metal ion increases with increasing alkyl substitution. As in his article no further discussion was given about the origin of this empirical rule, it hardly attracted the attention of other chemists at all. Recently, however, the same problem was taken up again by Parry and Keller, who noticed

15) N. V. Sidgwick, *J. Chem. Soc.*, **1941**, 433.
16) J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds", Chap. 3, R. W. Parry and R. N. Keller, "The Electronic Theory of Coordination Compounds", Reinhold Publishing Corporation, New York, (1956), p. 129.

a parallel relation between the coordinating ability of a donor group and its dipole moment and showed that Sidgwick's rule could be easily understood when the increasing or decreasing order of dipole moment of donor groups was taken into consideration. At the same time they showed that alkyl substitution caused a quite reverse effect on the magnitude of dipole moment between a series of hydrides of oxygen and nitrogen and a series of hydrides of sulfur and phosphorus, and they pointed out that the coordinating ability of phosphine derivatives increases in the order phosphine, ethyl phosphine, diethyl phosphine and triethyl phosphine,

Now let us turn our attention to the origin of the anomaly. The anomaly can not be explained by the variation of the valence angles of nitrogen and oxygen. For, the valence angle of nitrogen is nearly equal to 110° in ammonia[17], dimethylamine[19] and trimethylamine[20], and hence the valence angle in monomethylamine is presumed also to be nearly equal to 110°. Similarly, the valence angle of oxygen is nearly equal to 110° in water[17] and in dimethyl ether[21], and hence the valence angle of oxygen in alcohol is also supposed to be nearly equal to 110°. Besides, the anomaly appears also in the case of fluorides, where no valence angle can be considered. Accodingly we must consider another kind of origin. As the inductive effect is a very useful concept in understanding various chemical properties of organic compounds, the complete abandonment of this concept may only cause confusion. Far from abandonment, we must rather conclude that this anomaly has a close relation to the inductive effect, because the order of the magnitudes of dipole moments in a series is not irregular but strictly reverse to that which is expected from the consideration of the inductive effect. Therefore we take the view that the inductive effect exists in every kind of molecule. Consequently there should be the bond polarity induced by the inductive effect even in alcohols and amines, and this bond polarity should increase with successive alkyl substitution. Therefore, besides the bond polarity, we should assume another kind of component of the dipole moment which decreases reversely to the bond polarity with successive alkyl substitution. Frank[22] and Higasi[23] independently noticed this and attributed the variation of the dipole moment in a homologous series to the induction of alkyl groups by the primary dipole. They successfully gave the following interpretation to the systematic increase or decrease of the dipole moment in a homologous series with increasing alkyl substitution: Put the angle between the direction of the primary dipole and the line joining the center of the polarisable alkyl group and the center of the primary dipole θ. When the angle θ is below 60°, the secondary dipole is induced in the same sense as that of the primary one, and as a result the whole dipole moment increases with increasing alkyl substitution. On the contrary, when the angle θ exceeds 60°, the induced dipole has an opposite sense to the primary dipole, and hence the whole dipole moment decrease with increasing alkyl substitution. The series of alkyl chlorides, bromides and iodides belong to the former case, and the series of alcohols and amines to the latter case. This interpretation seems to be obviously reasonable. However, when we examine the data carefully, we meet several difficulties which can be by no means overcome by the theory of such a simple induction. In the first place, let us compare the data for three homologous series of alkyl chlorides, bromides and iodides. If the variation of the dipole moment in a homologous series were mainly due to the simple induction in the growing chain by the primary dipole between the carbon and halogen atoms, these three series should all show the same effect. That is, as the dipole moment of methyl halides rises in the order iodide, bromide and chloride, the dipole moment of ethyl, propyl and butyl halides should rise in the same order. The actual order is, however, iodide, chloride and bromide in these cases. In addition, as is seen in Table I, while methyl substitution in hydrogen chloride, bromide and iodide causes a marked increase in the dipole moment, the same substitution in hydrogen fluoride causes reversely the decrease in the dipole moment. The theory of induction can not give any reasonable suggestion to the

17) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. van Nostrand Co. Inc., New York (1945), p. 439.
18) ibid., p. 489.
19) S. H. Bauer, *J. Am. Chem. Soc.*, **60**, 524 (1938).
20) L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.*, **58**, 2036 (1936).
21) H. A. Stuart, *Z. Physik.*, **59**, 13 (1929).
22) H. Frank, *Proc. Roy. Soc.*, **A152**, 171 (1935).
23) K. Higasi, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **28**, 284 (1936).

interpretation of this fact. Further, let us compare the two cases of methylamine and ethylamine series. As the secondary dipole moment induced in the ethyl group should be larger than that induced in the methyl group in every case, and as such a secondary dipole should have an opposite sense to the primary dipole in an amine molecule, all methylamines should have a larger dipole moment than the corresponding ethylamines. This expectation is fulfilled in the cases of primary and secondary amines; the dipole moments of monomethylamine and dimethylamine are both larger than those of the corresponding monoethylamine and diethylamine. However, the dipole moment of trimethyl amine is smaller than that of triethylamine. This fact can not be explained by the theory of induction.

Therefore, in order to overcome these difficulties, we must seek for a component of the dipole moment quite different from the above-mentioned induced dipole moment. Such a component should be rather predominant in an anomalous series of compounds and decrease reversely to the bond polarity with the increasing $-I$ substitution. The atom dipole moment may be regarded as such a component. According to Coulson's calculation[24], the main part of the dipole moments of water and ammonia comes from "the atom dipole moment" produced by localization of electronic clouds which is caused by *s-p* hybridization of non-bonding electrons of oxygen and nitrogen, and the bond polarity contributes a little to the whole dipole moment. Thus we may assume the whole dipole moment μ_m consists of the bond polarity μ_b and the atom dipole moment μ_a;

$$\mu_m = \mu_a + \mu_b$$

Such an *s-p* hybridization of non-bonding electrons is considered to take place to a considerable extent especially in the hydrides of nitrogen, oxygen and fluorine and their derivatives. This may be presumed from the fact that the valence angle of nitrogen and oxygen is nearly equal to 110°. On the contrary, in compounds of elements below the third period in the periodic table such an *s-p* hybridization hardly ever takes place. This is presumed from the fact that the valence angles of sulfur[18] and phosphorus[25] are both near to 90°.

24) C. A. Coulson, *Proc. Roy. Soc.*, **A 207**, 63 (1951).
25) D. P. Stevenson, *J. Chem. Phys.*, **8**, 285 (1940).

Now let us apply the above interpretation to methylamine and ethylamine series. Since the $-I$ effect of ethyl is greater than that of methyl, the bond polarity of monoethylamine is greater than that of monomethylamine. The actual moment is, however, smaller in ethylamine than in methylamine. Further, compare the case of monoethylamine with that of dimethylamine. As the bond polarity of a secondary amine is much greater than that of a primary amine, we must assume that the atom dipole moment of primary amine is much greater than that of secondary amine, in order to explain the nearly equal dipole moments of monoethylamine and dimethylamine.

Thus we have obtained the following conclusion. *The more $-I$ active a substituent is, the more the degree of s-p hybridization decreases, and hence the more the contribution of the atom dipole moment to the whole dipole moment decreases.* In addition, it must be noted that such a decrease of hybridization may have its own limit. As already stated, the dipole moment of monoethylamine is much smaller than that of monomethylamine. This suggests that the decrease of the degree of hybridization takes place to a much greater extent in the case of methyl substitution. But the introduction of the second and third ethyl groups no longer causes a great decrease of the whole dipole moment, and in this respect an ethylamine series forms a contrast to a methylamine series. This change of dipole moments in an ethylamine series may be explained as follows. In an ethylamine series, as a result of a considerably great decrease of the degree of hybridization by the introduction of the first ethyl group, the introduction of the further ethyl groups brings about the increase of the bond polarity rather than the decrease of the degree of hybridization. Consequently no marked stepwise decrease of the dipole moment which appears in a methylamine series, is observed. Similarly in the case of fluorides, the decrease of the degree of hybridization approaches to its limit at the change from hydrogen fluoride to methyl fluoride, and the further $-I$ substitution brings about the increase of the bond polarity rather than the decrease of the atom dipole moment, so that the dipole moment of ethyl fluoride rises again from that of methyl fluoride. This interpretation is illustrated in Fig. 2.

Thus we have established the rule that

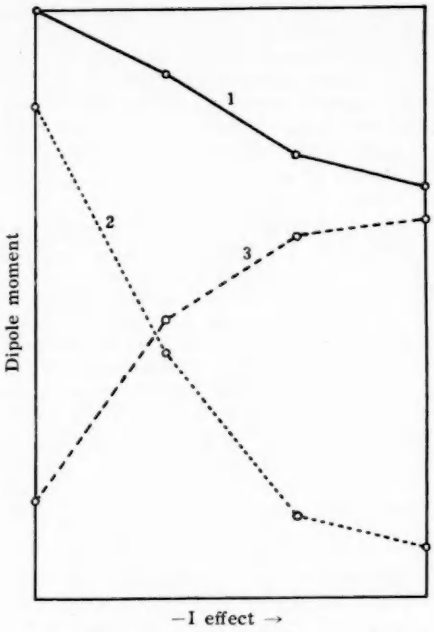

Fig. 2. Illustration of variation of the components of the dipole moment with successive −I substitution.
1 —— whole dipole moment
2 ····· atom dipole moment
3 - - - bond dipole moment

the introduction of the −I substituent prevents *s-p* hybridization of non-bonding electrons. If this rule is true, it should hold well not only for alkyl substitution, but also for any kind of substitution. Consequently, the introduction of the +I substituent should promote the *s-p* hybridization and hence increase the atom dipole moment. Therefore we can expect a large atom-dipole moment in hydrazine and hydroxylamine. But the problem is complicated in these cases. Because, these molecules consist of two parts which contribute equally or nearly equally to the whole dipole moment. These two parts make the restricted oscillation[26] near the trans positions, so that there occurs the compensation of the dipole moments of these two parts. This compensation is complete when the two parts are in the trans positions and becomes partial as they go away from the trans positions. Therefore unless the potential energy of oscillation is determined, we can not estimate the dipole moment of each part from the observed dipole moment. Therefore at present we can not prove directly the validity of the present view. With respect to the strong interaction between these molecules and metal ions, we have following evidences. Previously amine complexes of nickel(II), platinum(II) and cobalt(III) having various amines as ligands, were studied spectrochemically by the present author[27]. The result obtained shows that the affinity of amines toward these metal ions increases in the following order; ethylamine, methylamine, ethanolamine, ammonia and hydroxylamine. This series is the same as the order of the inductive effect of substituents, and the position of hydroxylamine in this series means the strong affinity toward metal ions, which indicates the large atom dipole moment of nitrogen in hydroxylamine. Further, according to Schwarzenbach's measurement[28] the consecutive formation constants of hexahydrazine nickel(II) complex are much larger than the corresponding consecutive formation constants of hexammine nickel(II) complex. This fact suggests that the atom dipole moment of nitrogen is much greater in hydrazine than in ammonia.

In addition, we can give a quite new interpretation to the unusal stability of ethylenediamine complexes. They have a great stability which can by no means be explained by the fact that they have a small probability with which a chelating agent leaves simultaneously two coordination positions. Further it must be noted that the characteristic absorption bands of ethylenediamine complexes of nickel(II), copper(II), cobalt(III), platinum(II) etc. lie in the wavelength shorter than those of the corresponding ammonia- and methylamine complexes. According to the crystal field theory[29], such characteristic absorption bands of transition metal complexes are due to the energy transitions between the split *d*-levels. As the energy intervals between the split d-levels increase with the increase of the electrostatic field set up by the ligands, it can be concluded that the stronger the field by the ligand is, the more the absorption bands of the complex appear in the shorter wavelength. Accordingly,

26) S. Mizushima, K. Higasi and Y. Morino, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **25**, 159 (1934); *Phys. Z.*, **35**, 905 (1934).

27) H. Yoneda, This Bulletin, **30**, 130 (1957); **30**, 924 (1957).

28) G. Schwarzenbach and A. Zobrist, *Helv. Chim. Acta*, **35**, 1291 (1952).

29) For example, L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

the above-mentioned fact indicates that the electric field toward the *d*-electrons which is produced by the ligands is stronger in ethylenediamine complexes than in ammonia- and methylamine complexes, and that the atom dipole moment of ethylenediamine is greater than that of ammonia and methylamine. Such an increased atom dipole moment of ethylenediamine can be explained as being due to a result of the mutual +I effect of the two amino groups within the molecule. The difference of the coordinating abilities between mono- and poly-alcohols[30] can also be explained in the same way.

Summary

As a result of the examination of dipole moments of hydrides of various elements and their alkyl derivatives the following regularity was found. Hydrides of elements below the third period in the periodic table show the normal variation of dipole moments with successive alkyl substitution. That is, the dipole moment increases with successive alkyl substitution, which is expected from the consideration of the inductive effect of substituents. On the other hand, hydrides of elements in the second period in the periodic table show the abnormal variation of dipole moments with successive alkyl substitution, which apparently seems to contradict the existence of the inductive effect. That is, the dipole moment decreases with successive alkyl substitution. This fact was connected with the concept of *s-p* hybridization of non-bonding electrons, and the following rule was drawn. The more −I active a substituent is, the more the degree of *s-p* hybridization of non-bonding electrons decreases, and hence the more the contribution of the atom dipole moment to the whole dipole moment decreases. Some applications of this rule to the chemistry of coordination compounds were also presented.

The author wishes to express his sincere thanks to Dr. M. Mashima of Saga University for his valuable discussions.

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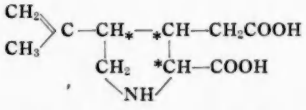
30) For example, M. Kubota, *J. Chem. Soc. Japan (Nippon Kagaku Kaisi)*, **61**, 1182 (1940).

*The Structure of Kainic Acid, the Most Active Component of Digenea Simplex Ag. II. The Molecular and Crystal Structure of Kainic Acid Monohydrate**

By Hideo WATASE, Yujiro TOMIIE and Isamu NITTA

(Received April 16, 1958)

As reported in the general survey[1] of our studies on the structures of kainic acid and its isomer, investigations based on X-ray crystal analysis were carried out. In the preceding paper[2] of this series, we already concluded that the structure of kainic acid, $C_{10}H_{15}O_4N$, was 2-carboxy-3-carboxymethyl-4-isopropenylpyrrolidine, and also determined the stereochemical configuration of the molecule from the structure of the kainate anion in the zinc salt.



However, it will be of still greater interest to determine the molecular structure of kainic acid in its own crystal, and thus to know how the molecular structures in the crystals of the salt and the free acid are related to each other.

The structure of the kainic acid crystal has been examined by two-dimensional

* Part of this paper was presented at the Autumnal Joint Meeting of Chemical Societies in Japan, Tokyo, 1956.

1) I. Nitta, H. Watase and Y. Tomiie, *Nature*, **181**, 761 (1958).

2) H. Watase and I. Nitta, This Bulletin, **30**, 889 (1957).

X-ray procedure. The electron-density projections along the three principal crystal axes were derived by the trial method, and the structure was determined. In this account, moreover, some general remarks on X-ray crystal analysis are added.

Experimental

Kainic acid crystallizes with one water molecule from its aqueous solution. Crystalline kainic acid monohydrate ($C_{10}H_{15}O_4N \cdot H_2O$) is composed of colorless thin needles elongated along a principal crystal axis (monoclinic b axis).

Oscillation-, Sauter- and Weissenberg-photographs, were taken about the three principal crystal axes, using Cu K_α radiation. The specimens used had the following cross-sections at right angles to the axis of rotation; 0.08×0.30 mm. for the b axis rotation, 0.15×0.6 mm. for the c axis and 0.4×0.5 mm. for the a axis**.

The intensity data for ($h0l$), ($hk0$) and ($0kl$) used in the two-dimensional analyses were taken from the integrated Weissenberg photographs for each zone. By comparing them with a calibrated scale, the intensities of the reflections were estimated visually, multiple-film technique being used for accurate measurements of strong reflections. The corrections for polarization and Lorentz factors were made in the usual way. The corrections for absorption and the form of the specimen were made only for ($hk0$) in an approximate way, the linear absorption coefficient for Cu K_α radiation being $\mu = 10.4/\text{cm}$***.

Relative structure factors were then deduced from these intensity data by the ordinary process.

Results and Discussion

Unit Cell and Space Group.—It was found from the X-ray examinations that the crystal belongs to the monoclinic system, and the dimensions of the unit cell are as follows;

$$a = 12.07 \pm 0.03 \text{ Å}$$
$$b = 5.86 \pm 0.02 \text{ Å}$$
$$c = 8.19 \pm 0.03 \text{ Å}$$
$$\beta = 94.7^\circ \pm 0.2^\circ.$$

Systematic absence of reflections being only ($0k0$) with k odd, the space group may be either $C_2^2 - P2_1$ or $C_{2h}^2 - P2_1/m$. However, since kainic acid is of an optically active compound, the space group is uniquely determined to be $C_2^2 - P2_1$ with no centers of symmetry. Judging from the cell size and the symmetry element of the crystal, it is clear that the unit cell contains two formula units of $C_{10}H_{15}O_4N \cdot H_2O$.

The axial period of b is short enough for a projection to provide useful information about the structure. Moreover, the two-fold screw axis lying parallel to this axis, the b axis projection is effectively centro-symmetrical. Therefore the determination of the structure was approached from the b axis projection.

Determination of the Structure.—As will be described in the last section of this paper, neither did the inequality method bring success in the present case, nor did the Patterson method give any information about the structure. On the other hand, we analyzed the zinc salt[2] and gave kainic acid the structure as mentioned previously (2-carboxy-3-carboxymethyl-4-isopropenylpyrrolidine). Adopting this structure, the trial method making use of the structure-factor maps for all the possible reflections of ($h0l$) was applied to locate all the atoms in the projection along the b axis.

Considering the packing, the probable position of the isopropenyl group could be roughly determined. Considering the various possible structures conceivable in connection with the position of the isopropenyl group, the signs of the structure factors of the lowest order except for those of small F values could be determined, and it was known that the absolute structure-factor values are close to those which are obtained from Wilson's method[3]. Then, determining the signs of the structure factors, the quantitative trial was carried on step by step from the lower to the higher orders so as to obtain a good agreement between the calculated and the observed F values, until all the atoms were located satisfactorily to permit the Fourier refinements. The final electron-density projection of Fig. 1 was thus derived, and the atomic positions were further refined from this map. The x and z atomic parameters were thus obtained.

In order to estimate the unknown y parameters, the projection along the c axis was investigated, using the structure-factor data of ($hk0$). Since this projection has no center of symmetry, differing from the case of the centro-symmetrical b axis projection, each structure factor consists of real and imaginary parts. By the trial use of the structure-factor maps for the

** To take the photographs about the a and c axes, the specimens were prepared by cutting the crystals at right angles to the needle axis (b axis).

*** This value comes from the unit cell containing two formula units. (see next section).

3) A. J. C. Wilson, *Acta Cryst.*, **2**, 318 (1949).

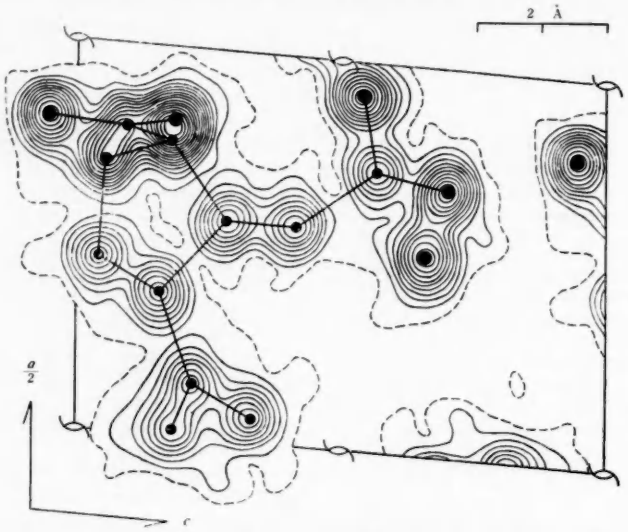


Fig. 1. The final electron-density projection along the *b* axis. Contour lines are at unit electron intervals, the lowest line, broken line, being 1 electron per Å^2. Black circles show the final atomic positions, there being large, intermediate and small circles for oxygen, nitrogen and carbon respectively.

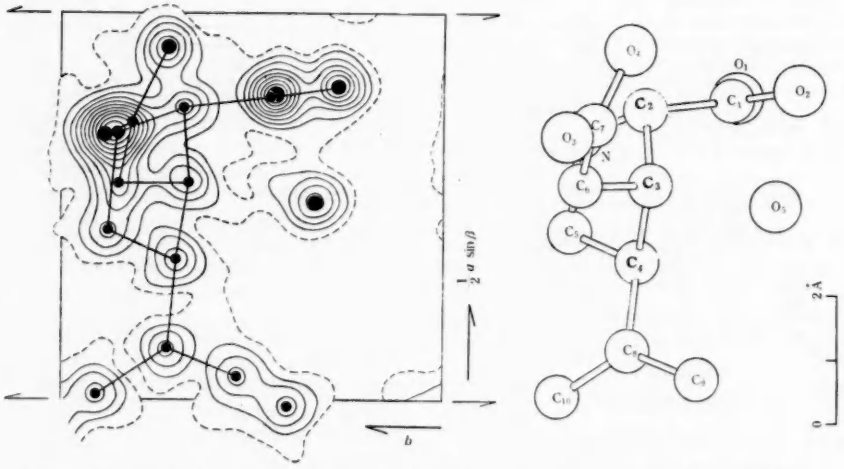


Fig. 2. The final electron-density projection along the *c* axis. Contour lines are at two electrons intervals, the lowest line, broken line, being 2 electrons per Å^2. Black circles show the atomic positions, there being large, intermediate and small circles for oxygen, nitrogen and carbon respectively. The interpretation of the density map is given on the right side.

lower order reflections only, the *y* parameters of all the atoms were easily obtained, and these parameters were further refined by the Fourier refinements. In this trial, since for a weak reflection, both the real and the imaginary part of the structure factor should be small, the structure-factor maps of the weak reflections were most useful. The final electron-density projection along the *c* axis was thus derived as shown in Fig. 2. The final *x*, *y* and *z* atomic parameters are listed in Table I.

The phases of the structure factors for

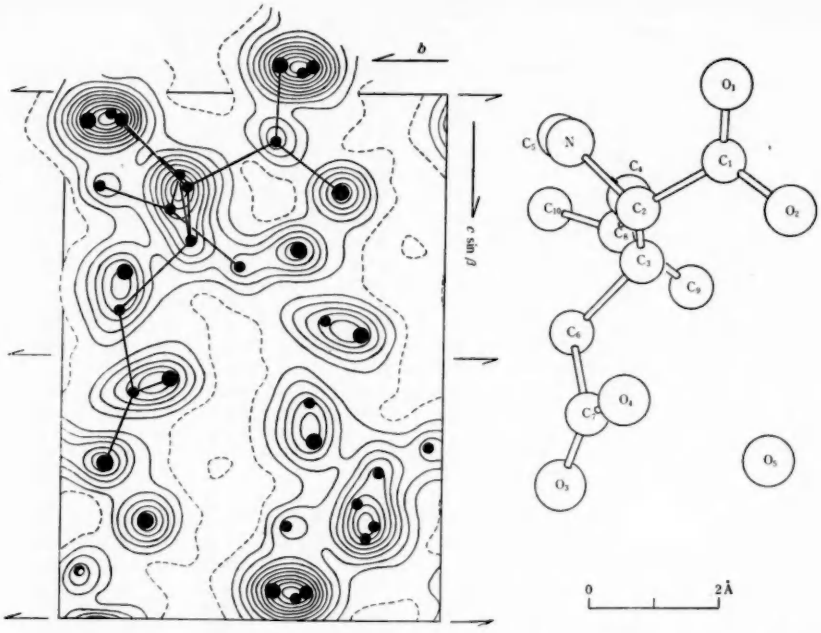


Fig. 3. The final electron-density projection along the *a* axis. Contours and symbols are the same as those of Fig. 2. The interpretation of the density map is given on the right side.

(0*kl*) were calculated from the *y* and *z* atomic parameters, and the electron-density projection along the *a* axis was obtained as shown in Fig. 3.

TABLE I
ATOMIC PARAMETERS

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C_1	0.393	0.451	0.094
C_2	0.379	0.679	0.178
C_3	0.282	0.667	0.282
C_4	0.183	0.698	0.158
C_5	0.222	0.878	0.042
C_6	0.281	0.850	0.415
C_7	0.360	0.815	0.567
C_8	0.069	0.722	0.220
C_9	0.030	0.540	0.332
C_{10}	0.008	0.908	0.182
N	0.347	0.855	0.053
O_1	0.397	0.438	0.943
O_2	0.405	0.277	0.185
O_3	0.344	0.887	0.704
O_4	0.458	0.719	0.540
O_5 (H_2O)	0.257	0.337	0.658

At this stage, the discrepancy indices ($R=\sum||F_o|-|F_c||/\sum|F_o|$) are 0.175 for (*h*0*l*), 0.159 for (*hk*0) and 0.244 for (0*kl*), employing the data up to $\sin\theta/\lambda=0.625$ for (*h*0*l*) and 0.640 for (*hk*0) and (0*kl*), assuming the values of the unobserved structure factors to be precisely zero and neglecting the contributions from hydrogen atoms. In the structure-factor calculations, the effect of thermal motion was taken into account, the value of $B=3.0$ Å^2 being used for each zone as the temperature factor common to all the atoms. The atomic scattering factors were taken from McWeeny's paper[4]; for oxygen $f_0=1/3(f^{\parallel}+2f^{\perp})$ and for carbon the values for 'valence states'.

The observed and the calculated structure factors for (*h*0*l*) are listed in Table II, and those for (*hk*0) and (0*kl*) in Table III.

Molecular Structure.—The bond lengths and bond angles, calculated from the atomic parameters of Table I, are shown in Fig. 4. It may be said that the bond lengths will be correct to ±0.03Å and the bond angles to ±3°. As a result, it was confirmed that the structure of kainic acid is 2-carboxy-3-carboxymethyl-4-isopropenylpyrrolidine in agreement with the structure determined from that of the

4) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS $F(h0l)$

$h\ k\ l$	$1/2F_o$	$1/2F_c$	$h\ k\ l$	$1/2F_o$	$1/2F_c$	$h\ k\ l$	$1/2F_o$	$1/2F_c$	$h\ k\ l$	$1/2F_o$	$1/2F_c$
0 0 0	—	124	1 0 4	2.8	4.4	4 0 9	1.0	1.0	13 0 $\bar{4}$	—	0.6
1 0 0	20.0	−23.1	2 0 4	—	−1.0	5 0 9	—	0.4	14 0 $\bar{4}$	2.1	2.9
2 0 0	5.2	− 5.2	3 0 4	2.7	2.7	6 0 9	2.3	− 1.9	1 0 5	2.6	4.6
3 0 0	29.8	29.8	4 0 4	2.1	−2.0	0 0 10	1.0	− 1.1	2 0 5	7.2	6.7
4 0 0	3.2	− 5.4	5 0 4	4.4	−4.3	1 0 10	—	1.0	3 0 5	12.1	−12.6
5 0 0	15.8	15.6	6 0 4	2.4	3.2	2 0 10	1.3	− 1.0	4 0 5	5.6	6.9
6 0 0	5.0	− 4.6	7 0 4	6.8	−7.4	1 0 $\bar{1}$	11.2	10.1	5 0 5	3.4	4.8
7 0 0	2.5	− 1.9	8 0 4	2.7	2.8	2 0 $\bar{1}$	2.6	4.2	6 0 5	4.7	−4.8
8 0 0	3.2	5.1	9 0 4	1.9	−0.7	3 0 $\bar{1}$	13.3	13.5	7 0 5	1.8	−2.0
9 0 0	3.5	− 3.9	10 0 4	2.9	−2.9	4 0 $\bar{1}$	16.0	−15.8	8 0 5	2.3	−1.9
10 0 0	0.8	− 0.5	11 0 4	—	−0.7	5 0 $\bar{1}$	24.1	22.4	9 0 5	—	−1.2
11 0 0	3.3	3.3	12 0 4	1.9	−1.2	6 0 $\bar{1}$	3.7	3.9	10 0 5	2.3	2.6
12 0 0	—	− 0.3	13 0 4	2.3	2.8	7 0 $\bar{1}$	4.4	− 3.8	11 0 5	2.1	−2.6
13 0 0	—	− 0.2	0 0 5	—	0.5	8 0 $\bar{1}$	11.1	10.2	12 0 5	—	0.4
14 0 0	—	− 0.2	1 0 5	—	1.0	9 0 $\bar{1}$	5.3	− 6.3	13 0 5	—	0.0
15 0 0	1.5	2.3	2 0 5	1.9	−2.3	10 0 $\bar{1}$	3.2	4.2	1 0 $\bar{6}$	6.7	6.7
0 0 1	7.7	7.7	3 0 5	8.5	9.4	11 0 $\bar{1}$	—	0.2	2 0 $\bar{6}$	2.7	−1.7
1 0 1	13.2	−12.6	4 0 5	6.1	−5.9	12 0 $\bar{1}$	1.9	1.1	3 0 $\bar{6}$	2.8	2.9
2 0 1	1.0	− 2.6	5 0 5	—	0.3	13 0 $\bar{1}$	1.2	1.4	4 0 $\bar{6}$	4.0	4.2
3 0 1	9.6	− 8.5	6 0 5	1.8	0.7	14 0 $\bar{1}$	—	0.1	5 0 $\bar{6}$	1.8	2.6
4 0 1	14.3	−14.7	7 0 5	2.3	2.7	15 0 $\bar{1}$	1.3	1.6	6 0 $\bar{6}$	3.0	3.1
5 0 1	13.1	11.5	8 0 5	2.3	1.8	1 0 $\bar{2}$	5.4	5.7	7 0 $\bar{6}$	3.3	4.4
6 0 1	6.6	− 8.0	9 0 5	1.3	−0.8	2 0 $\bar{2}$	14.1	−13.5	8 0 $\bar{6}$	5.4	−5.0
7 0 1	3.7	− 4.1	10 0 5	1.2	1.3	3 0 $\bar{2}$	0.7	− 1.9	9 0 $\bar{6}$	3.2	3.1
8 0 1	5.7	− 6.0	11 0 5	2.5	2.8	4 0 $\bar{2}$	12.2	− 9.4	10 0 $\bar{6}$	1.2	0.9
9 0 1	2.8	3.1	12 0 5	—	0.3	5 0 $\bar{2}$	1.8	− 2.5	11 0 $\bar{6}$	1.9	−1.9
10 0 1	7.0	7.4	0 0 6	1.2	2.6	6 0 $\bar{2}$	9.5	6.9	12 0 $\bar{6}$	—	1.4
11 0 1	6.6	− 8.0	1 0 6	0.8	−0.5	7 0 $\bar{2}$	4.3	− 4.0	1 0 $\bar{7}$	1.0	−0.8
12 0 1	2.2	2.4	2 0 6	4.7	4.2	8 0 $\bar{2}$	3.7	− 4.9	2 0 $\bar{7}$	1.0	−1.3
13 0 1	1.2	1.8	3 0 6	5.4	−4.6	9 0 $\bar{2}$	5.6	5.6	3 0 $\bar{7}$	—	0.4
14 0 1	—	− 0.9	4 0 6	2.3	2.3	10 0 $\bar{2}$	2.3	− 2.6	4 0 $\bar{7}$	1.0	0.0
0 0 2	4.7	− 5.6	5 0 6	3.3	4.0	11 0 $\bar{2}$	1.9	− 2.7	5 0 $\bar{7}$	3.3	−4.0
1 0 2	34.5	−35.9	6 0 6	—	−1.0	12 0 $\bar{2}$	2.3	− 2.1	6 0 $\bar{7}$	6.6	7.6
2 0 2	9.9	12.0	7 0 6	1.3	−1.4	13 0 $\bar{2}$	2.1	2.4	7 0 $\bar{7}$	1.9	1.3
3 0 2	15.9	−15.0	8 0 6	5.7	5.4	14 0 $\bar{2}$	—	− 0.8	8 0 $\bar{7}$	—	−0.6
4 0 2	5.3	3.4	9 0 6	—	−0.8	15 0 $\bar{2}$	1.6	− 1.3	9 0 $\bar{7}$	—	0.3
5 0 2	6.2	4.6	10 0 6	—	−0.9	1 0 $\bar{3}$	3.7	3.9	10 0 $\bar{7}$	—	1.5
6 0 2	7.5	− 6.6	11 0 6	1.2	1.5	2 0 $\bar{3}$	14.2	−14.3	11 0 $\bar{7}$	2.9	2.9
7 0 2	1.6	− 0.5	0 0 7	—	−0.7	3 0 $\bar{3}$	1.7	− 2.2	1 0 $\bar{8}$	7.0	5.9
8 0 2	5.4	5.1	1 0 7	—	−0.9	4 0 $\bar{3}$	10.6	10.0	2 0 $\bar{8}$	—	−0.8
9 0 2	0.8	0.5	2 0 7	4.8	−4.1	5 0 $\bar{3}$	13.6	−13.6	3 0 $\bar{8}$	10.2	−8.2
10 0 2	0.8	0.6	3 0 7	1.0	−0.4	6 0 $\bar{3}$	1.5	1.0	4 0 $\bar{8}$	1.3	0.3
11 0 2	1.9	2.0	4 0 7	1.0	0.6	7 0 $\bar{3}$	1.6	− 0.2	5 0 $\bar{8}$	1.0	−1.5
12 0 2	1.8	− 2.4	5 0 7	1.0	−0.7	8 0 $\bar{3}$	0.8	− 0.1	6 0 $\bar{8}$	3.0	−3.2
13 0 2	—	0.1	6 0 7	—	−0.5	9 0 $\bar{3}$	1.8	1.9	7 0 $\bar{8}$	1.7	0.7
14 0 2	—	0.0	7 0 7	1.2	−0.3	10 0 $\bar{3}$	1.9	− 1.4	8 0 $\bar{8}$	2.2	−2.0
0 0 3	1.5	0.4	8 0 7	1.1	−1.2	11 0 $\bar{3}$	2.7	− 2.5	9 0 $\bar{8}$	—	0.2
1 0 3	1.3	0.9	9 0 7	—	0.3	12 0 $\bar{3}$	—	1.5	10 0 $\bar{8}$	0.8	−1.4
2 0 3	17.0	−15.4	10 0 7	1.1	−2.0	13 0 $\bar{3}$	2.0	− 2.8	1 0 $\bar{9}$	—	0.8
3 0 3	17.8	17.0	0 0 8	9.7	−7.8	14 0 $\bar{3}$	—	0.2	2 0 $\bar{9}$	3.8	3.3
4 0 3	1.9	2.1	1 0 8	1.3	0.1	1 0 $\bar{4}$	9.8	− 8.5	3 0 $\bar{9}$	2.3	−1.9
5 0 3	1.4	0.0	2 0 8	—	−0.5	2 0 $\bar{4}$	6.5	6.9	4 0 $\bar{9}$	1.6	2.3
6 0 3	1.6	− 1.5	3 0 8	—	0.3	3 0 $\bar{4}$	3.3	− 3.1	5 0 $\bar{9}$	3.7	−4.0
7 0 3	2.9	− 3.3	4 0 8	4.3	3.6	4 0 $\bar{4}$	—	− 0.6	6 0 $\bar{9}$	—	0.0
8 0 3	3.6	4.8	5 0 8	4.2	−4.5	5 0 $\bar{4}$	2.2	− 2.8	7 0 $\bar{9}$	1.3	1.1
9 0 3	1.9	1.1	6 0 8	2.2	1.7	6 0 $\bar{4}$	3.0	− 2.0	8 0 $\bar{9}$	3.2	−2.7
10 0 3	5.2	− 5.6	7 0 8	—	0.6	7 0 $\bar{4}$	3.0	3.6	1 0 $\bar{10}$	—	−0.7
11 0 3	1.8	− 1.2	8 0 8	1.2	−1.6	8 0 $\bar{4}$	6.3	− 8.5	2 0 $\bar{10}$	1.7	2.1
12 0 3	—	− 0.4	0 0 9	2.0	−1.6	9 0 $\bar{4}$	6.5	6.4	3 0 $\bar{10}$	1.2	1.2
13 0 3	2.5	− 2.7	1 0 9	2.0	2.1	10 0 $\bar{4}$	—	0.5	4 0 $\bar{10}$	—	−0.1
14 0 3	1.3	0.8	2 0 9	—	0.5	11 0 $\bar{4}$	—	0.2			
0 0 4	0.9	− 0.3	3 0 9	—	0.3	12 0 $\bar{4}$	1.2	0.6			

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ($hk0$) AND ($0kl$)

The values for ($h00$) and ($00l$) are listed in Table II.

h k l	$1/2F_o$	$1/2F_c$	h k l	$1/2F_o$	$1/2F_c$	h k l	$1/2F_o$	$1/2F_c$	h k l	$1/2F_o$	$1/2F_c$
1 1 0	22.1	23.2	6 3 0	2.8	4.6	1 6 0	1.5	2.2	0 3 2	3.8	5.7
2 1 0	3.2	4.8	7 3 0	1.9	2.3	2 6 0	4.1	4.2	0 3 3	9.3	10.5
3 1 0	9.6	12.1	8 3 0	2.8	2.6	3 6 0	1.1	0.8	0 3 4	5.8	5.9
4 1 0	10.9	11.8	9 3 0	2.0	2.1	4 6 0	2.8	2.7	0 3 5	2.1	2.8
5 1 0	10.6	9.8	10 3 0	3.9	5.2	5 6 0	2.2	2.2	0 3 6	4.4	3.5
6 1 0	1.9	2.5	11 3 0	1.5	0.5	6 6 0	2.1	2.0	0 3 7	4.0	4.1
7 1 0	13.8	13.8	12 3 0	2.2	1.9	7 6 0	1.9	1.4	0 3 8	1.0	2.4
8 1 0	13.2	12.7	13 3 0	1.4	0.8	8 6 0	0.9	1.5	0 3 9	1.3	0.6
9 1 0	4.1	3.8	14 3 0	1.2	0.4	9 6 0	1.3	1.9	0 4 1	3.5	6.0
10 1 0	5.8	4.4	0 4 0	7.3	6.2	1 7 0	3.0	2.2	0 4 2	4.3	0.8
11 1 0	2.3	3.1	1 4 0	2.3	2.0	2 7 0	2.2	1.5	0 4 3	5.3	7.5
12 1 0	3.4	3.9	2 4 0	8.8	9.1	3 7 0	2.0	2.1	0 4 4	0.6	2.2
13 1 0	3.9	4.2	3 4 0	5.3	5.4	4 7 0	1.2	1.0	0 4 5	1.6	1.9
14 1 0	1.0	1.0	4 4 0	2.9	3.3	5 7 0	1.2	0.6	0 4 6	1.0	0.7
15 1 0	2.0	2.5	5 4 0	3.0	3.5	0 1 1	17.3	17.5	0 4 7	1.4	1.2
0 2 0	26.9	28.3	6 4 0	3.1	2.8	0 1 2	9.5	8.9	0 4 8	1.4	1.1
1 2 0	14.3	13.4	7 4 0	2.0	1.2	0 1 3	10.5	10.8	0 5 1	5.1	4.6
2 2 0	8.3	11.0	8 4 0	3.6	3.0	0 1 4	7.3	8.2	0 5 2	1.9	4.9
3 2 0	15.1	15.2	9 4 0	3.0	2.5	0 1 5	5.5	5.4	0 5 3	0.6	2.2
4 2 0	1.9	3.5	10 4 0	2.8	3.0	0 1 6	10.8	9.5	0 5 4	1.5	2.7
5 2 0	5.0	6.2	11 4 0	1.7	1.4	0 1 7	1.1	2.1	0 5 5	0.6	0.5
6 2 0	2.6	3.1	12 4 0	1.8	0.9	0 1 8	3.4	2.1	0 5 6	1.6	2.6
7 2 0	3.4	2.9	13 4 0	1.2	2.5	0 1 9	2.1	1.5	0 5 7	2.3	1.4
8 2 0	7.2	6.4	1 5 0	6.3	7.4	0 1 10	0.4	0.3	0 6 1	1.0	2.1
9 2 0	3.2	3.0	2 5 0	6.7	7.0	0 2 1	6.7	11.0	0 6 2	0.6	0.8
10 2 0	1.7	2.5	3 5 0	1.3	2.0	0 2 2	13.1	9.3	0 6 3	0.7	1.6
11 2 0	2.9	3.2	4 5 0	—	1.0	0 2 3	16.8	15.1	0 6 4	0.6	1.4
12 2 0	2.2	2.6	5 5 0	3.1	4.4	0 2 4	4.3	2.7	0 6 5	1.1	0.1
13 2 0	1.1	1.1	6 5 0	2.9	2.2	0 2 5	6.8	5.4	0 6 6	0.4	1.3
14 2 0	1.9	1.3	7 5 0	4.3	3.3	0 2 6	3.2	2.9	0 7 1	1.9	2.4
1 3 0	0.9	0.9	8 5 0	2.7	1.1	0 2 7	1.2	2.1	0 7 2	1.4	1.2
2 3 0	4.1	4.9	9 5 0	2.3	1.3	0 2 8	3.1	3.6	0 7 3	1.2	1.2
3 3 0	3.7	6.1	10 5 0	1.9	0.9	0 2 9	0.6	0.8			
4 3 0	5.4	7.0	11 5 0	1.7	1.3	0 2 10	1.0	0.6			
5 3 0	5.6	7.0	0 6 0	2.2	3.8	0 3 1	5.8	4.4			

kainate anion in the zinc salt[2] and also with the conclusion deduced from the chemical evidences[5].

The observed lengths of the bonds except for the C—O distances are in agreement within ±0.03 Å with those of the corresponding bonds in the kainate anion, the differences being not definitely significant, if the errors be taken into consideration, while some of the bond angles are fairly different from those of the kainate anion.

The C—O distances of the carboxymethyl group of C_3 are found to be 1.23 Å for C_7—O_3 and 1.34 Å for C_7—O_4, owing presumably to the formations of the hydrogen bonds involved (Fig. 9). The oxygen O_4 is of the hydroxyl group (OH). The C—O distances of the carboxyl group of C_2 are 1.24 Å for C_1—O_1 and 1.27 Å for C_1—O_2, being also due to hydrogen bond formations. The dimensions of this group are in good agreement with those of the CH_2COO^- group in the kainate anion (1.24 and 1.28 Å) or with those of the COO^- groups in similar hydrogen-bonded cases; hydroxyproline (1.25 and 1.27 Å)[6] and hexamethylene-diammonium adipate (1.24 and 1.28 Å)[7].

5) M. Miyasaki, *J. Pharm. Soc. Japan* (Yakugaku Zasshi), **75**, 695 (1955); Y. Ueno, H. Nawa, J. Ueyanagi, H. Morimoto, R. Nakamori and T. Matsuoka, ibid., **75**, 840 (1955); S. Murakami, T. Takemoto, Z. Tei and K. Daigo, ibid., **75**, 869 (1955).

6) J. Zussman, *Acta Cryst.*, **4**, 493 (1951); J. Donohue and K. N. Trueblood, ibid., **5**, 419 (1952).

7) S. Hirokawa, T. Ohashi and I. Nitta, *Acta Cryst.*, **7**, 87 (1954).

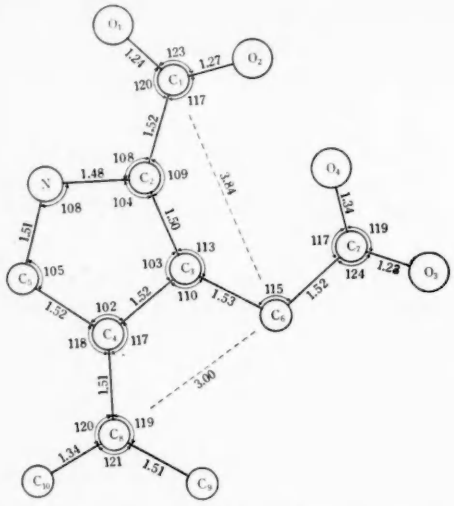


Fig. 4. Bond lengths (Å) and bond angles (°).

Judging from the dimensions of the carboxyl group of C_2 and the consideration about the observed hydrogen bonds (Fig. 9), at least in crystalline state, the kainic acid molecule is considered to be of the 'zwitter ion' structure in which the carboxyl group of C_2 is of COO^- and the nitrogen is of N^+H_2, although the positions of no hydrogen atoms are located in the present work. The infrared spectrum of this crystal also suggests the existence of the ionized carboxyl group, showing the absorption at 6.20 μ[8].

The stereochemical relations of the atoms in kainic acid molecule are in agreement with those of the kainate anion. Namely, the carboxyl group of C_2 and the carboxymethyl group of C_3 take the *trans*-configuration relative to the ring, and the latter group and the isopropenyl group of C_4 are in the *cis*-configuration. This fact supports the reasoning based on chemical evidences[9]. In the isopropenyl group, the double bond C_8—C_{10} is so located as to be more close to the ring than the single bond C_8—C_9 as in the case of the kainate anion. The stereochemical configuration of the molecule is shown in Fig. 5.

Owing mainly to the *cis*-configuration of the two side-chains attached to the neighboring C_3 and C_4, the five-membered pyrrolidine ring (N, C_2, C_3, C_4, C_5) is considerably distorted from the planar form as it is in the case of the kainate anion, their valence angles being remarkably deviated from the ordinary values. The distance between C_6 and C_8 is found to be 3.00 Å, a value similar to 2.96 Å in the kainate anion. As seen clearly in Fig. 3, the four atoms N, C_2, C_4 and C_5 of the pyrrolidine ring are approximately lying on one plane, and the carbon atom C_3 is shifted from the plane of the other four by about 0.6 Å, much greater than about 0.4 Å of the similar displacement in hydroxyproline[6]. The mode of the deformation of the pyrrolidine ring is different in the kainate anion due presumably to the difference of crystalline field, the pyrrolidine ring being thus found to be fairly flexible. In the case of the kainate anion, the carbon atom C_5 is displaced much farther from the mean plane than the other four.

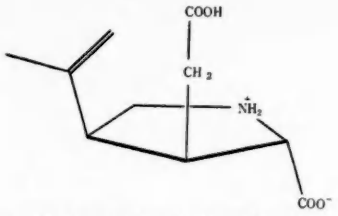


Fig. 5. Stereochemical configuration.

Finally, in Fig. 6, the molecule of kainic acid is indicated by the model which is derived from the atomic parameters of the present X-ray analysis, viewed along the *b* axis.

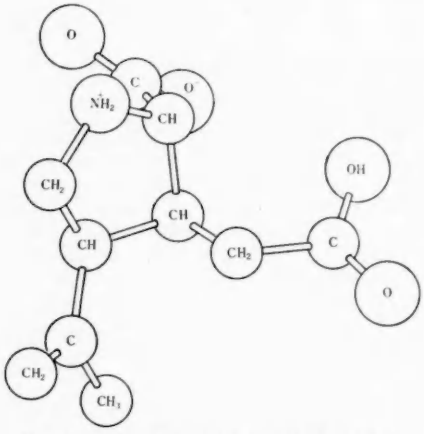


Fig. 6. The arrangement of the atoms in kainic acid, viewed along the *b* axis.

8) Y. Ueno, H. Nawa, J. Ueyanagi, H. Morimoto, R. Nakamori and T. Matsuoka, *J. Pharm. Soc. Japan* (Yakugaku Zasshi), **75**, 807 (1955).

9) H. Morimoto and R. Nakamori, *J. Pharm. Soc. Japan* (Yakugaku Zasshi), **76**, 294 (1956); *Proc. Japan Acad.*, **32**, 41 (1956); T. Takemoto, Z. Tei and K. Daigo, *J. Pharm. Soc. Japan* (Yakugaku Zasshi), **76**, 298 (1956).

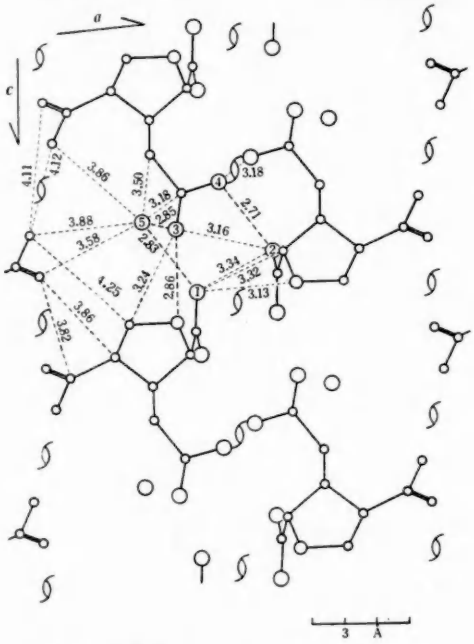


Fig. 7. View of the crystal structure along the *b* axis. The intermolecular distances are shown in Å. Large circles represent oxygens, intermediate nitrogens and small carbons.

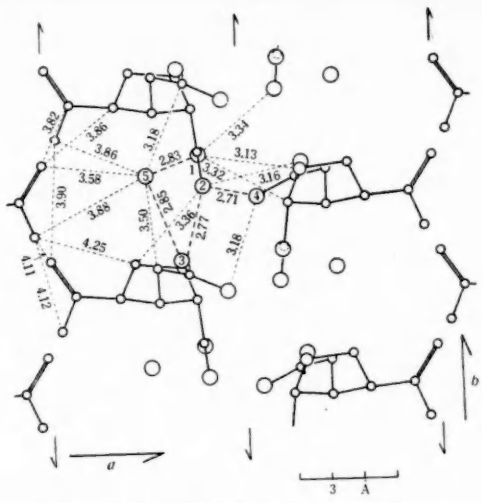


Fig. 8. View of the crystal structure along the *c* axis. The intermolecular distances are shown in Å. Symbols are the same as those of Fig. 7.

Crystal Structure. — The views of the crystal structure along the *b*, *c* and *a* axes are illustrated in Figs. 7, 8 and 9 respectively, giving the intermolecular distances. The space group being C_2^2—$P2_1$, the crystal has only two-fold screw axes parallel to the *b* axis as the symmetry element. The unit cell contains two molecules of kainic acid and two waters, the kainic acid molecule being the zwitter ion of which the account is given in the last section. As a whole, the crystal structure is a layered one, like those of the zinc salt[2] or allokainic acid[10].

There are five kinds of short intermolecular distance of 2.71~2.86 Å between oxygens or oxygen and nitrogen, and the intermolecular hydrogen bonds are considered to be formed there. The two hydrogens of N^+H_2 form the intermolecular hydrogen bonds between the nitrogen and the oxygen O_2 of the carboxyl group $(COO)^-$ or the oxygen O_3 of the carboxymethyl group. These hydrogen bond distances are 2.77 Å for N—H···O_2 and 2.86 Å for N—H···O_3. The hydrogen attached to the oxygen O_4 of the carboxymethyl group also forms the hydrogen bond between the molecules, its O_4—H···O_2 distance being 2.71 Å. The water which is packed into the crystal to fill the space links one molecule to another by forming two hydrogen-bridges between the water oxygen O_5 and two molecules. They are O_5—H···O_1 of 2.83 Å and O_5—H···O_3 of 2.85 Å. The hydrogen bond angles are given in Fig. 9.

The projection along the *a* axis (Fig. 9) shows well how one molecule is linked to others by the hydrogen bonds. By these hydrogen bonds, the molecules and the waters are linked to each other infinitely, forming a double layered structure parallel to the (100) plane. In the projections along the *b* and *c* axes (Figs. 7 and 8), it is clearly seen that between the double layers the nonpolar groups or atoms are in contact with each other, the distances of the closest approach being 3.82 Å for C_8···C_{10}, 3.86 Å for C_4···C_{10}, 4.11 Å for C_9···C_{10} and 4.12 Å for C_9···C_9. This is compatible with the observed cleavage parallel to the (100) plane.

Some Remarks on X-ray Crystal Analysis

In order to derive the *b* axis electron-density projection, the analysis based on

10) H. Watase, to be published.

TABLE IV

SIGN RELATIONS AND CORRECT SIGNS (+OR−)

ξ	(3 0 0) +	(1 0 $\bar{4}$)*−		$-ad\xi$	(3 0 6) −		
η	(8 0 $\bar{1}$) +			acd	(2 0 $\bar{8}$) −		
$\xi\eta$	(5 0 $\bar{1}$) +	(3 0 5) −		$acd\eta$	(4 0 1)*−		
a	(0 0 8) −	(2 0 $\bar{4}$) +	(8 0 2) +	$acd\xi\eta$	(1 0 1) −	(3 0 5) +	
$a\xi$	(3 0 $\bar{8}$) −			ae	(6 0 $\bar{6}$) +		
$a\eta$	(2 0 7) −	(8 0 $\bar{9}$) −		$b\xi$	(5 0 0) +		
$a\xi\eta$	(3 0 3) +	(5 0 $\bar{9}$) −		$c\xi$	(1 0 8) +	(3 0 $\bar{4}$) −	
ab	(8 0 8) −			$c\eta$	(2 0 3) −		
$ab\xi$	(5 0 8) −			$cd\xi\eta$	(5 0 1) +	(5 0 $\bar{3}$)*−	
$ac\xi$	(1 0 0) −			d	(2 0 $\bar{10}$) +	(4 0 $\bar{6}$) +	
$ac\eta$	(4 0 $\bar{1}$) −			$d\xi$	(1 0 $\bar{6}$) +		
ad	(2 0 $\bar{2}$) −	(4 0 2) +		$d\eta$	(4 0 5) −	(6 0 $\bar{7}$) +	
$ad\xi$	(1 0 2) −	(9 0 $\bar{4}$) +		$e\xi$	(3 0 2) −		
$ad\eta$	(4 0 $\bar{3}$) +	(6 0 1) −		−	(4 0 8) +		
$ad\xi\eta$	(3 0 1) −			+	(8 0 6) −		

* These were determined by Sayre's method.

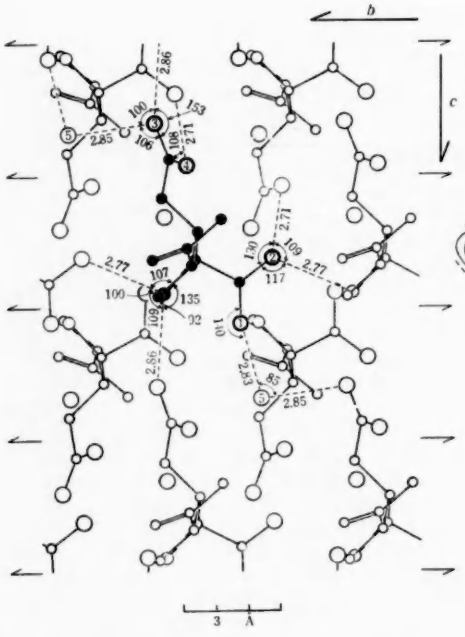


Fig. 9. View of the crystal structure along the a axis. The hydrogen bonds about one molecule are shown by broken lines, their distances (Å) and angles (°) being given. Symbols are the same as those of Fig. 7.

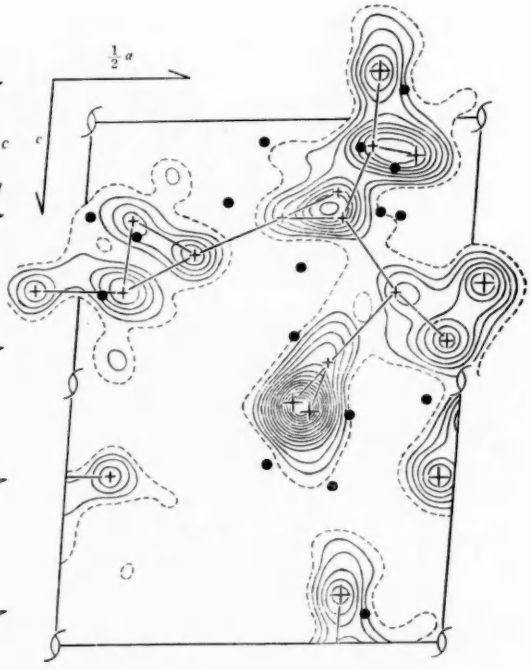


Fig. 10. Projection of incorrect electron-density on (010). Contours are drawn at equal intervals on an arbitrary scale, the lowest contour, broken line, being drawn at zero level of Fourier summations. Cross-symbols indicate the incorrect atomic positions considered from this map, there being large, intermediate and small symbols for oxygen, nitrogen and carbon respectively. The correct atomic positions are shown by black circles. An incorrect structure considered from this map is indicated by interatomic bonds.

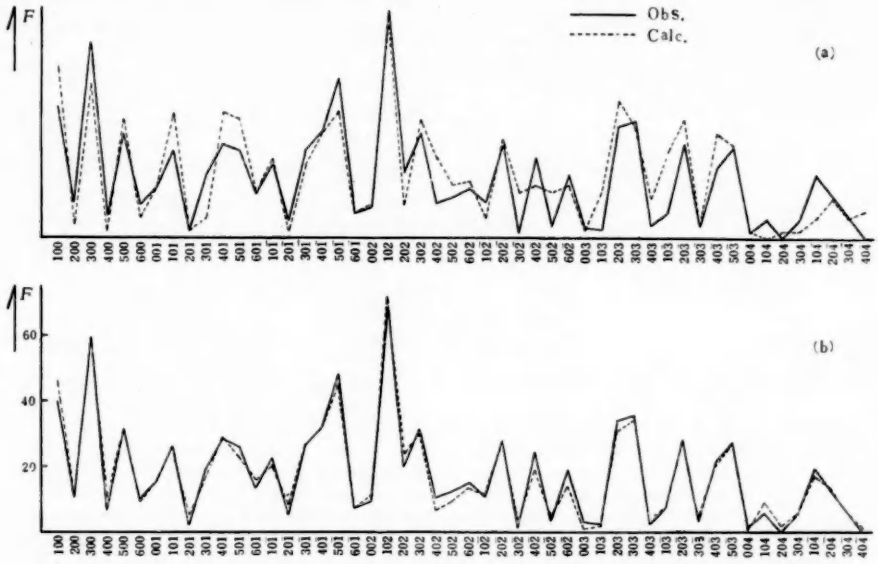


Fig. 11. F-values, (a) for the incorrect structure of Fig. 10, (b) for the correct structure of Fig. 1. The values for only fifty reflections of lower orders ($\sin\theta/\lambda < 0.29$) are shown.

direct methods was first attempted, because the crystal of kainic acid contains no heavy atom, and, furthermore, the chemical structure was entirely unknown when this work began.

The Harker-Kasper inequalities[11] was applied to obtain the sign relations of the structure factors for ($h0l$), using Sakurai's chart[12]. Unitary structure factors $U(h0l)$ were calculated from the relative structure factors $F'(h0l)$, as follows:

$$U(h0l),\ K=|F'(h0l)|\exp B(\sin\theta/\lambda)^2/\Sigma f_i$$

where f_i is the atomic scattering factor[13] of the ith atom. The scale factor K and the temperature factor B were obtained by Wilson's method[3].

However, since by this procedure sign relations could not be given because of low magnitudes of the unitary structure factors, an attempt was made to determine sign relations of some terms as in the case of the analysis of sodium tropolonate[14]. Namely, the unitary structure factors were multiplied by an artificial constant of about 1.3, and the sign relations of 44 terms were then obtained without contradiction by the Harker-Kasper inequalities. In addition, these relations were also checked by Sayre's method[15]. These sign relations together with the correct signs for the structure of Fig. 1 are listed in Table IV, where ξ and η are arbitrary parameters[16].

By the Fourier method based on these signs and further trial-and-error, an electron-density map was derived as shown in Fig. 10, the sign relations of Table IV being satisfied except for only four reflections with small F value. From this map a structure might be guessed by connecting reasonably with the peaks found as indicated also in Fig. 10. However, the R index calculated on this structure was about 40%, and it seemed impossible to decrease the R value satisfactorily by the further refinement of this map. Moreover, even in the lower order, some of the calculated structure factors showed considerable discrepancy from their observed values as shown in Fig. 11 (a); for example (301), (402), (10$\bar{3}$), (10$\bar{4}$), etc. We gave up this map, Fig. 10, considering that it was wrong, being of a 'false structure'. When

11) D. Harker and J. S. Kasper, *Acta Cryst.*, **1**, 70 (1948).
12) K. Sakurai, ibid., **5**, 546 (1952).
13) "Internationale Tabellen zur Bestimmung von Kristallstrukturen", Bornträger, Berlin (1935).
14) Y. Sasada and I. Nitta, *Acta Cryst.*, **9**, 205 (1956).
15) D. M. Sayre, ibid., **5**, 60 (1952).
16) Y. Okaya and I. Nitta, ibid., **5**, 564 (1952).

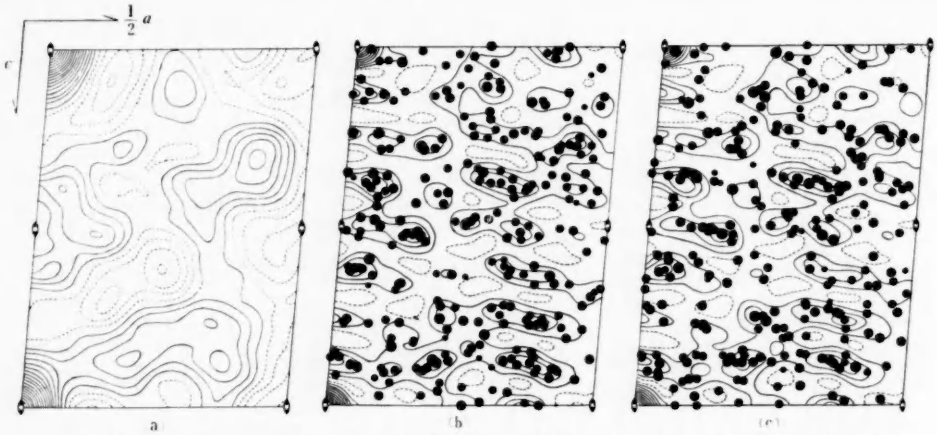


Fig. 12. The Patterson function projected on (010), a) ordinary function, b) and c) modified function to obtain sharp peaks. Contours of each map are drawn at equal intervals on an arbitrary scale, the lowest solid line being drawn at zero level of Fourier summations. Black circles of the maps b) and c) show the positions of the Patterson peaks, b) derived from the correct structure of Fig. 1, c) derived from the incorrect structure of Fig. 10. The area of each black circle is approximately proportional to the weight of the peak.

the correct structure was next determined, it was revealed that the sign relations obtained above were quite random ones, as shown in Table IV, though the above inequalities gave apparently consistent relations.

In the present case, thirty-two atoms are in the unit cell excluding hydrogen atoms, and, generally speaking, this number of atoms per unit cell is too many for the inequality method to be applied. A successful application of the inequality method to tropolone hydrochloride[17] has been reported, the unit cell of which contains forty atoms. However, there are four heavy chlorine atoms which are distinguishable from others, and the signs obtained by this method coincide with those of the contributions from the chlorine atoms except for only one structure factor with a small F value.

Although there is the fortunate case of sodium tropolonate, it must be borne in mind that the sign relations obtained by raising artificially the scale of unitary structure factors may not necessarily correspond to the true structure and even may lead to a false structure as in the present case. It generally seems that the more atoms are contained in a unit cell, the more various false structures will be possible.

As for the application of the Patterson method, the ordinary Patterson function $P(x, z)$ was first calculated, and further to obtain sharp peaks a modified Patterson function $P'(x, z)$ was also calculated as follows:

$$P'(x, z) = k \sum_{h} \sum_{l} U(h0l)^2 \cos 2\pi(hx + lz)$$

where k is the scale factor. Both projection maps are shown in Fig. 12. However, no useful information about the structure was provided from these maps. Even in such a case, this function may be applicable as a method to check whether or not a derived structure is correct, as seen from a comparison between the maps b and c of Fig. 12. If a structure derived by any other method is correct, the Patterson map should be quantitatively interpreted as shown in the map b of Fig. 12.

We wish to express our thanks to Professor-Emeritus S. Murakami, Dr. T. Takemoto and their collaborators of this University and Drs. S. Kuwada, S. Tatsuoka, Y. Ueno and their collaborators of the Research Laboratory of Takeda Pharmaceutical Industry, Ltd. for supplying the specimens and kindly discussing problems with us. Thanks are also due to Dr. H. Tani, Mr. Y. Sasada and Mr. T. Shiba of this University for helpful advice and continued interest. Appreciation is

17) Y. Sasada, K. Osaki and I. Nitta, ibid., **7**, 113 (1954).

also expressed to Messrs. S. Sakakibara, M. Okumiya and Miss K. Koike of this University for their help in microanalyses.

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A Study of Tin Oxides by X-Ray Diffraction Method

By Kichizo NIWA, Iwao YAMAI and Tsuguyasu WADA

(Received March 31, 1958)

There are various reports available for the occurrence and stability of tin oxides: stannous oxide, β-stannous oxide, tritin tetroxide and stannic oxide. Most of these reports are in accord with one another on the point that stannous oxide decomposes into tin and stannic oxide at higher temperatures, though various temperatures have been reported for the decomposition such as 400°C[1], 510°C[2], 385°C[3] and 300°C.[4] Weiser and Milligan[5], however, showed that heating of stannous oxide in vacuo at 500°C gives a product which is neither stannous oxide, nor tin and stannic oxide and which they called β-stannous oxide.

According to Spandau and Kohlmeyer[6,7] stannous oxide decomposes into tin and tritin tetroxide over the temperature range from about 400°C to 1040°C, the melting point of stannous oxide. On the other hand, Platteeuw and Meyer[4] have recently reported that stannous oxide on heating in vacuo at 300°C and 550°C completely decomposed into tin and stannic oxide.

Owing to the results of the measurements on equilibria of $Sn—SnO_2—CO—CO_2$[8] and $Sn—SnO_2—H_2—H_2O$[9] the existence of β-stannous oxide and tritin tetroxide as stable compounds is improbable in the temperature range about 550°C to 850°C. But Fraenkel and Snipischski[2] deduced from an equilibrium measurement that some compound other than stannous oxide and stannic oxide existed above 900°C.

The thermodynamic data obtained by Veselovsky[10] indicate that stannous oxide (solid) is stable only within temperature range about 300° to 600°K. But recent calorimetric determination of the heat of formation of the tin oxides performed by Humphrey and O'Brien[11] indicates that stannous oxide (solid) is unstable over all temperature ranges.

In this work, a change of stannous oxide by heating, observed by X-ray diffraction methods, is reported and discussion is offered as to the existence of β-stannous oxide or tritin tetroxide and the decomposition of stannous oxide.

Experimental

Materials.—Stannous oxide was prepared by adding sodium hydroxide solution to a hydrochloric acid solution of stannous chloride until the solution became slightly alkaline and by boiling the resulting mixture until the precipitate turned black. The black stannous oxide precipitate was decanted until it became free from chloride; then it was dried at 110°C for eighteen hours. Stannic oxide was prepared by drying and calcining the white metastannic acid obtained by the reaction of concentrated nitric acid with metallic tin. X-ray diffraction patterns obtained from these two oxides were in agreement with the previous data, and no other impurities were observed.

Heating of stannous oxide, and tin-

1) M. Staumanis and C. Strek, *Z. anorg. u. allgem. Chem.*, **213**, 310 (1933).
2) W. Fraenkel and K. Snipischski, ibid., **125**, 235 (1922).
3) C. G. Fink and C. L. Mantel, *J. Phys. Chem.*, **32**, 103 (1928).
4) J. C. Platteeuw and G. Meyer, *Trans. Faraday Soc.*, **52**, 1066 (1956).
5) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **36**, 3039 (1932).
6) H. Spandau and E. G. Kohlmeyer, *Z. anorg. u. allgem. Chem.*, **254**, 65 (1947).
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8) E. D. Eastman and R. Robinson, *J. Am. Chem. Soc.*, **50**, 1106 (1928).
9) P. H. Emmett and J. F. Shultz, ibid., **55**, 1390 (1933).
10) B. K. Veselovsky, *J. Appl. Chem.* (U. S. S. R.), **16**, No. 9/10, 397 (1943); *Chem. Abst.*, **38**, 6148 (1944).
11) G. L. Humphrey and C. J. O'Brien, *J. Am. Chem. Soc.*, **75**, 2805 (1953).

stannic oxide mixture.—One- to two-tenths grams of sample were sealed in Pyrex tube in vacuo at 100°C or in nitrogen gas at 1/3 atmosphere. Each tube was heated in an electric furnace for a given time, then quenched to room temperature and cut for opening. The contents were examined by X-ray diffraction method, using Cu$K\alpha$ ray in a Debye-Scherrer camera of 90 mm. diameter.

High temperature X-ray diffraction.—A high temperature camera (Rigaku-Denki Co.) was used to obtain the patterns at elevated temperature by using Cu$K\alpha$-ray. The samples were sealed in a Pyrex capillary in vacuo.

Results

The diffraction patterns obtained from the quenched samples are illustrated in Fig. 1, A—C, corresponding to No. 6—8 in Table I. In Table I, the results of analysis of patterns, which were obtained from the sample quenched after treatment at various temperatures (column 3) and durations (column 4), are listed. No other compounds than tin, stannous oxide and stannic oxide were observed. Results of heating in nitrogen agree with those in vacuo.

TABLE I

RESULTS OF HEATING OF SnO AND A MIXTURE OF Sn AND SnO_2

Sample No.	Initial Sample	Temperature °C	Time min.	Detected Substances SnO	Sn	SnO_2
1	SnO	550	3	−	++	++
2	〃	〃	10	−	++	++
3	〃	〃	75	−	++	++
4	〃	〃	180	−	++	++
5	Sn+SnO_2	〃	75	−	++	++
6	SnO	500	5	++	+	+
7	〃	〃	10	+	+	+
8	〃	〃	15	−	++	++
9	〃	450	60	+	++	++
10	〃	〃	120	−	++	++
11	〃	400	600	++	+	+
12	Sn+SnO_2	〃	〃	−	++	++

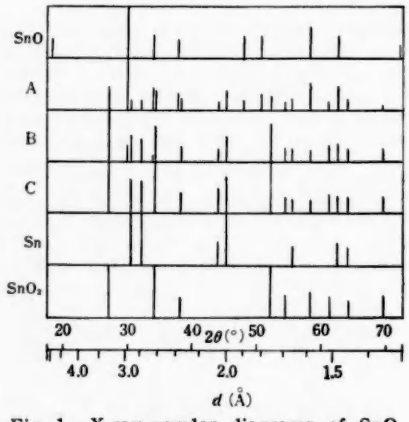

Fig. 1. X-ray powder diagrams of SnO heated at 500°C.

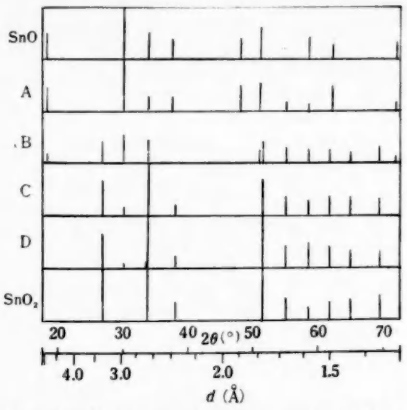

Fig. 2. X-ray powder diagrams of SnO heated at 445°C and 500°C, obtained by high temperature camera.

The patterns obtained by the high temperature camera are shown in Fig. 2. Fig. 2-D gives schematic pattern for thirty minutes of exposure at 500°C, where the material was ascertained only as stannic oxide. Fig. 2-A, -B and -C are patterns which were obtained step-by-step at 445°C. At each step forty minutes of exposure are needed. The pattern 2-A reveals the presence of monoxide and a small amount of dioxide; 2-B, monoxide and a comparable amount of dioxide; and 2-C, dioxide and a very small amount of monoxide, respectively.

Discussion

When stannous oxide is heated at 550°C in vacuo, the decomposition reaction,

$$2SnO \rightarrow Sn + SnO_2$$

is completed in a relatively short time. The reaction is also completed in the same manner at 500°C and 450°C, though the reaction time is prolonged. At 400°C, a certain small amount of stannous oxide still remains even after a considerably long time of heating. But reverse reaction started from tin and stannic oxide does not proceed at all. From these facts, it is deduced that the decomposition reaction may be completed even at 400°C, though the reaction velocity is very slow.

TABLE II

COMPARISON BETWEEN β-SnO* AND A MIXTURE OF Sn, SnO_2 AND SnO

β-SnO*		Sn		SnO_2		SnO		Corresponding
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	Substance
						(4.81	1)	
3.38	10	—	—	3.34	10	—	—	SnO_2
2.99	5	—	—	—	—	2.97	4	SnO
2.92	5	2.91	7	—	—	—	—	Sn
2.88	9	2.80	5	—	—	—	—	Sn ?
2.66	9	—	—	2.64	7	2.66	1	SnO_2
				(2.36	2)	(2.39	f)	
2.08	1	2.05	2	—	—	—	—	Sn
2.02	4	2.01	5	—	—	—	—	Sn
						(1.89	f)	
1.77	8	—	—	1.75	7	1.79	1	SnO_2
1.67	2	1.65	2	1.67	2	—	—	Sn & SnO_2
1.59	2	—	—	1.58	1	1.59	2	SnO_2 & SnO

* Obtained by Weiser and Milligan.

d: Spacing *I*: Intensity f: Faint

The patterns obtained by the high temperature X-ray diffraction camera show that the quenched samples sufficiently represent the high temperature state. In this temperature tin exists in liquid phase and hence gives no lines.

The conclusion is that, in the temperature range from 550°C to 400°C stannous oxide is thermodynamically unstable and decomposes into tin and stannic oxide.

As shown in Table II, the pattern of β-stannous oxide which was obtained by Weiser and Milligan is very similar to that of a mixture of tin, stannous oxide and stannic oxide except for minor disagreements. However, the pattern of stannous oxide reported by the same authors is found to be slightly inconsistent with the other authors' data. Further, Weiser and Milligan found the color of β-stannous oxide to be gray. This color is the same as that of the mixture of tin, stannous oxide and stannic oxide, but does not agree with the deep orange color of β-stannous oxide, which was prepared by two different methods by Partington and Moser[12]. It is presumed, therefore, that β-stannous oxide observed by Weiser and Milligan was not a new phase, but substantially a mixture of tin, stannous oxide and stannic oxide.

The existence of tritin tetroxide in equilibrium, which was deduced by Spandau at high temperatures, is rather open to question, since stannous oxide completely decomposes into tin and stannic oxide at high temperatures. Since patterns other than those of stannous oxide and stannic oxide were observed and no change in lattice-spacings was detected in the patterns obtained by a high temperature camera, it is clear that the coexistence of tin, stannous oxide and stannic oxide is not stable, and that they form neither a new phase nor a solid solution. The experiments by Spandau were carried out in a nitrogen-gas stream. But it is hardly probable that nitrogen has any influence on the decomposition, since the results of heating of stannous oxide in nitrogen agree with those in vacuo.

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Electronic States of p-Benzoquinone. III. Calculation of the Out-of-plane Vibrational Frequencies in the Ground Electronic State

By Tosinobu ANNO and Akira SADÔ*

(Received March 31, 1958)

In the first[1] and the second[2] part of this series the present authors, in collaboration with Matubara, have calculated the energy levels of *p*-benzoquinone using the semiempirical molecular orbital method proposed by Pariser and Parr[3], taking account of non-bonding electrons explicitly as well as π electrons. Experimental checking of the theoretical results requires the vibrational analysis of the electronic band spectrum of this molecule. To this end, the assignment of fundamental frequencies to modes of vibrations in the ground electronic state should be made at first.

Although the calculation of the fundamental frequencies using the force constants carried over from similar molecules would help those assignments using infrared and Raman data, the force constants to be carried over for *p*-benzoquinone are nearly unknown, since the normal coordinate treatments of quinones have not been performed yet.

In a recent paper[4] by one of the present authors, a method of obtaining some of the out-of-plane force constants in conjugated hydrocarbons from bond orders and of borrowing the remaining kinds of these constants from similar molecules was described. In the present paper the result of calculation of the non-planar frequencies of *p*-benzoquinone using this method will be reported.

Group-Theoretical Considerations

The molecular structure of *p*-benzoquinone has been studied by both the X-ray and electron-diffraction[6] experiments and it is known that this molecule belongs to the point group V_h. We take the axis connecting the two oxygen atoms as y axis and the molecular plane as xy plane. Then, the symmetry notations are the same as those given by Herzberg[7].

The fundamental vibrations of this molecule are distributed among symmetry species as follows; $6A_g+5B_{1g}+1B_{2g}+3B_{3g}+2A_u+3B_{1u}+5B_{2u}+5B_{3u}$. Vibrations in species B_{2g}, B_{3g}, A_u and B_{1u} are non-planar ones and the remaining vibrations are of planar modes.

Internal Coordinates and G Matrix

Notations for internal and symmetry coordinates are chosen to be as consistent as possible with those of benzene[8,9].

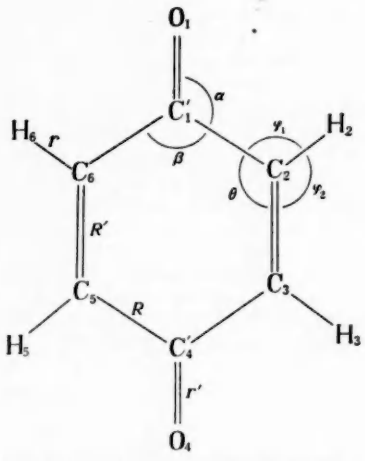

Fig. 1. Notations expressing bond angles and bond distances and the numbering of atoms for *p*-benzoquinone.

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6) S. M. Swingle, *J. Am. Chem. Soc.*, **76**, 1409 (1954).
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9) Y. Kakiuti and T. Shimanouchi, ibid., **25**, 1252 (1956).

Thus, as shown in Fig. 1 the carbon atoms are numbered consecutively, and the oxygen and the hydrogen atoms are numbered altogether consecutively. The carbon atom to which an oxygen atom attaches is distinguished by being primed. Equilibrium internuclear distances are represented by: $C_1'O_1=r'$, $C_2H_2=r$, $C_1'C_2=R$, and $C_2C_3=R'$, as also shown in Fig. 1, together with the notations for bond angles. The internal coordinates used are chosen as follows: the perpendicular displacement of the ith hydrogen(oxygen) atom out of the plane defined by the three nearest carbon atoms is termed $r\gamma_i$ ($r'\gamma_i'$); the out-of-plane ring bendings are regarded as torsions around carbon-carbon bonds; carbon atoms 1, 2, and 3 define one plane and carbon atoms 2, 3, and 4 define another; these planes intersect along the C_2C_3 bond; the angle between them is designated δ_2', prime denoting that the angle refers to a nominal double bond; for the corresponding quantities referring to a "single bond" the prime is dropped.

Table I contains symmetry coordinates formed from internal coordinates described above. In benzene, symmetry coordinates corresponding to S_A, S_B, and S_C are redundant. In the case of *p*-benzoquinone, however, S_A and S_C are not redundant by themselves. Therefore, we retain them in the following calculation and a frequency of zero is found in each of the cases of species A_u and B_{3g}.

Following Wilson's[10] procedure we obtain the factorized **G** matrix whose elements are given in Table II. Although **G**-matrix elements given in Table II are expressed as generally as possible in conformity with V_h structure, we need the internuclear distances and bond angles in order to calculate the numerical values of these elements. The following values are used: $r=1.08$ Å, $r'=1.23$ Å, $R=1.461$ Å, $R'=1.349$ Å, $\alpha=\theta=122°$, and $\beta=116°$. These are the values determined by electron-diffraction experiment[6] except R, R', and r. The values of CC distances are those calculated from bond order rather than experimental values, because when we later estimate the frequencies in the excited electronic states, the CC length will also be obtained from bond order. The CH distance assumed is taken from benzene[11]. Moreover, the C_2H_2 bond, for example, is assumed to bisect the external angle between bonds $C_1'C_2$ and C_2C_3. Therefore, it follows $\varphi_1=\varphi_2=119°$. The values of bond orders used are those calculated by a semiempirical MO method taking CI into account. Just as in the case of the calculation of the energy levels[2] not only the singly-excited configurations but also the doubly-excited configurations were considered, although only the "more important configurations" were taken into the secular equation and the neglected configurations were considered by the second-order perturbation theory. Bond orders obtained are:

$$p_{C_1'C_2}=0.226 \text{ and } p_{C_2C_3}=0.945.$$

Potential Function

Notations for valence force constants are also chosen as consistently as possible with those for benzene[8,9]. Fig. 2 shows **F** matrix in terms of internal coordinates.

	$r'\gamma_1'$	$r\gamma_2$	$r\gamma_3$	$r'\gamma_4'$	$r\gamma_5$	$r\gamma_6$	$R\delta_1$	$R'\delta_2'$	$R\delta_3$	$R\delta_4$	$R'\delta_5'$	$R\delta_6$
$r'\gamma_1'$	A''	a_o'	a_m'	a_p''	a_m'	a_o'	c_o'	c_m''	c_p'	$-c_p'$	$-c_m''$	$-c_o'$
$r\gamma_2$		A	a_o	a_m'	a_p	a_m	$-c_o$	$\bar{c}_o$	$c_m{}^d$	c_p	$-\bar{c}_p$	$-c_m{}^s$
$r\gamma_3$			A	a_o'	a_m	a_p	$-c_m{}^d$	$-\bar{c}_o$	c_o	$c_m{}^s$	$\bar{c}_p$	$-c_p$
$r'\gamma_4'$				A''	a_o'	a_m'	$-c_p'$	$-c_m''$	$-c_o'$	c_o'	c_m''	c_p'
$r\gamma_5$					A	a_o	c_p	$-\bar{c}_p$	$-c_m{}^s$	$-c_o$	$\bar{c}_o$	$c_m{}^d$
rr_6						A	$c_m{}^s$	$\bar{c}_p$	$-c_p$	$-c_m{}^d$	$-\bar{c}_o$	c_o
$R\delta_1$							B	b_o'	b_m	b_p	b_m'	b_o
$R'\delta_2'$		(Symmetric)						B''	b_o'	b_m'	b_p''	b_m'
$R\delta_3$									B	b_o	b_m'	b_p
$R\delta_4$										B	b_o'	b_m
$R'\delta_5'$											B''	b_o'
$R\delta_6$												B

Fig. 2. **F** matrix in terms of internal coordinate.

10) E. B. Wilson, Jr., ibid., **7**, 1047 (1939); **9**, 76 (1941).

11) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

TABLE
SYMMETRY COORDINATES IN TERMS

S_{16a}							
S_{17a}			$-1/2$	$1/2$		$-1/2$	$1/2$
S_A							
S_{11}		$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$
S_{16b}							
S_{17b}	=	$-2/\sqrt{12}$	$1/\sqrt{12}$	$1/\sqrt{12}$	$-2/\sqrt{12}$	$1/\sqrt{12}$	$1/\sqrt{12}$
S_{10a}			$1/2$	$1/2$		$-1/2$	$-1/2$
S_B							
S_4							
S_5		$1/\sqrt{6}$	$-1/\sqrt{6}$	$1/\sqrt{6}$	$-1/\sqrt{6}$	$1/\sqrt{6}$	$-1/\sqrt{6}$
S_{10b}		$-2/\sqrt{12}$	$-1/\sqrt{12}$	$1/\sqrt{12}$	$2/\sqrt{12}$	$1/\sqrt{12}$	$-1/\sqrt{12}$
S_G							

TABLE II

G-MATRIX ELEMENTS FOR THE OUT-OF-PLANE VIBRATIONS OF *p*-BENZOQUINONE

(Species A_u)

$G_{16a,16a}=(4\mu_C/3)(D+E-2F)^2$

$G_{17a,17a}=\mu_H+\mu_C(1+B+2C)^2$

$G_{A,A}=(2\mu_C/3)(D-2E-2F)^2$

$G_{16a,17a}=(2\sqrt{3}\,\mu_C/3)(D+E-2F)(1+B+2C)$

$G_{16a,A}=(2\sqrt{2}\,\mu_C/3)(D+E-2F)(D-2E-2F)$

$G_{17a,A}=(\sqrt{6}\,\mu_C/3)(1+B+2C)(D-2E-2F)$

(Species B_{1u})

$G_{11,11}=(\mu_O/3)+(2\mu_H/3)+(\mu_C/3)[(1+2A-2B)^2+2(1+B-A)^2]$

$G_{16b,16b}=3\mu_C(F+G-H)^2$

$G_{17b,17b}=(2\mu_O/3)+(\mu_H/3)+\mu_C(1+2A+B)^2$

$G_{11,16b}=(\sqrt{6}\,\mu_C)(F+G-H)(A-B)$

$G_{11,17b}=(\sqrt{2}/3)(\mu_H-\mu)_O-(\sqrt{2}\,\mu_C)(1+2A+B)(A-B)$

$G_{16b,17b}=-(\sqrt{3}\,\mu_C)(1+2A+B)(F+G-H)$

(Species B_{2g})

$G_{10a,10a}=\mu_H+\mu_C(1+B)^2$

$G_{B,B}=\mu_C(F+G+H)^2=0$

$G_{10a,B}=-\mu_C(1+B)(F+G+H)=0$

(Species B_{3g})

$G_{4,4}=(2\mu_C/3)[2(D-F-G+H)^2+(-D-2E+3F+G-H)^2]$

$G_{5,5}=(\mu_O/3)+(2\mu_H/3)+(\mu_C/3)[(1+2A+2B)^2+2(1+A+B+2C)^2]$

$G_{10b,10b}=(2\mu_O/3)+(\mu_H/3)+(\mu_C/3)[2(1+2A-B)^2+(1-2A+B+2C)^2]$

$G_{G,G}=(\mu_C/3)[2(H-G-F-2D)^2+(2D-2E-3F+G-H)^2]$

$G_{4,5}=(2\mu_C/3)[(D-F-G+H)(-1-2A-2B)+(-D-2E+3F+G-H)(1+A+B+2C)]$

$G_{4,10b}=(\sqrt{2}\,\mu_C/3)[2(D-F-G+H)(1+2A-B)+(-D-2E+G+3F-H)(1-2A+B+2C)]$

$G_{4,G}=(\sqrt{2}\,\mu_C/3)[2(D-F-G+H)(-2D-F-G+H)$
$+(-D-2E+3F+G-H)(2D-2E-3F+G-H)]$

$G_{5,10b}=(\sqrt{2}/3)(\mu_H-\mu_O)+(\sqrt{2}\,\mu_C/3)[(1-2A-2B)(1+2A-B)$
$+(1+A+B+2C)(1-2A+B+2C)]$

$G_{5,G}=(\sqrt{2}\,\mu_C/3)[(1+2A+2B)(2D+F+G-H)+(1+A+B+2C)(2D-2E-3F+G-H)]$

$G_{10b,G}=(\mu_C/3)[2(1+2A-B)(-2D-F-G+H)+(1-2A+B+2C)(2D-2E-3F+G-H)]$

$A=(r'\sin\alpha/R\sin\beta)$ $B=(r\sin\varphi_2/R\sin\theta)$ $C=(r\sin\varphi_1/R'\sin\theta)$ $D=R'/R\sin\theta$
$E=R/R'\sin\theta$ $F=\cos\theta/\sin\theta$ $G=\cos\beta/\sin\beta$ $H=1/\sin\beta$

μ_H, μ_C and μ_O are the reciprocal masses of the hydrogen, the carbon and the oxygen atom, respectively.

I
OF INTERNAL COORDINATES

$-1/\sqrt{12}$	$2/\sqrt{12}$	$-1/\sqrt{12}$	$-1/\sqrt{12}$	$2/\sqrt{12}$	$-1/\sqrt{12}$	$r'\gamma_1'$
						$r\gamma_2$
$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$r\gamma_3$
						$r'\gamma_4'$
$1/2$		$-1/2$	$1/2$		$-1/2$	$r\gamma_5$
						$r\gamma_6$
						$R\delta_1$
$1/2$		$-1/2$	$-1/2$		$1/2$	$R'\delta_2'$
$1/\sqrt{6}$	$-1/\sqrt{6}$	$1/\sqrt{6}$	$-1/\sqrt{6}$	$1/\sqrt{6}$	$-1/\sqrt{6}$	$R\delta_3$
						$R\delta_4$
						$R'\delta_5'$
$1/\sqrt{12}$	$2/\sqrt{12}$	$1/\sqrt{12}$	$-1/\sqrt{12}$	$-2/\sqrt{12}$	$-1/\sqrt{12}$	$R\delta_6$

TABLE III
FACTORIZED **F**-MATRIX ELEMENTS

(Species A_u)

$F_{16a,16a}=(1/3)(B+2B''-4b_o'+b_o-4b_m'+b_m+2b_p''+b_p)$
$F_{17a,17a}=A-a_o-a_m+a_p$
$F_{A,A}=(1/3)[2B+B''+2(b_o+2b_o')+2(b_m+2b_m')+2b_p+b_p'']$
$F_{16a,17a}=(1/\sqrt{3})(-c_o-2\bar{c}_o+c_m{}^d-c_m{}^s+c_p+2\bar{c}_p)$
$F_{16a,A}=(\sqrt{2}/3)(B''-B+b_o'-b_o+b_m'-b_m+b_p''-b_p)$
$F_{17a,A}=\sqrt{2/3}\,(c_o-\bar{c}_o-c_m{}^d+c_m{}^s-c_p+\bar{c}_p)$

(Species B_{1u})

$F_{11,11}=(1/3)[A''+2A+2(2a_o'+a_o)+2(2a_m'+a_m)+a_p''+2a_p]$
$F_{16b,16b}=B-b_o-b_m+b_p$
$F_{17b,17b}=(1/3)(2A''+A+a_o-4a_o'+a_m-4a_m'+a_p+2a_p'')$
$F_{11,16b}=\sqrt{2/3}\,(c_o'-c_o+c_m{}^s-c_m{}^d+c_p-c_p')$
$F_{11,17b}=(\sqrt{2}/3)(A-A''+a_o-a_o'+a_m-a_m'+a_p-a_p'')$
$F_{16b,17b}=(1/\sqrt{3})(-2c_o'-c_o-c_m{}^d+c_m{}^s+2c_p'+c_p)$

(Species B_{2g})

$F_{10a,10a}=A+a_o-a_m-a_p$

(Species B_{3g})

$F_{4,4}=(1/3)[2B+B''-2(2b_o'+b_o)+2(2b_m'+b_m)-(2b_p+b_p'')]$
$F_{5,5}=(1/3)[A''+2A-2(2a_o'+a_o)+2(2a_m'+a_m)-(a_p''+2a_p)]$
$F_{10b,10b}=(1/3)(2A''+A+4a_o'-a_o-4a_m'+a_m-2a_p''-a_p)$
$F_{C,C}=(1/3)(B+2B''+4b_o'-b_o-4b_m'+b_m-b_p-2b_p'')$
$F_{4,5}=(2/3)[(c_o'+c_o+\bar{c}_o)-(c_m''+c_m{}^d+c_m{}^s)+(c_p'+c_p+\bar{c}_p)]$
$F_{4,10b}=(\sqrt{2}/3)[(c_o+\bar{c}_o-2c_o')-(c_m{}^d+c_m{}^s-2c_m'')+(c_p+\bar{c}_p-2c_p')]$
$F_{4,C}=(\sqrt{2}/3)(B-B''+b_o'-b_o-b_m'+b_m+b_p''-b_p)$
$F_{5,10b}=(\sqrt{2}/3)(A-A''+a_o'-a_o-a_m'+a_m+a_p''-a_p)$
$F_{5,C}=(\sqrt{2}/3)[(c_o'+c_o-2\bar{c}_o)-(c_m{}^d+c_m{}^s-2c_m'')+(c_p'+c_p-2\bar{c}_p)]$
$F_{10b,C}=(1/3)[(-2c_o'-2\bar{c}_o+c_o)-(c_m{}^d+c_m{}^s+4c_m'')-(2c_p'-c_p+2\bar{c}_p)]$

The transformation from internal to symmetry coordinates yields the factorized **F** matrix whose elements are shown in Table III. Following the work on benzene by Kakiuti and Shimanouchi[9] only the interaction constants referring to such internal coordinates that are "ortho" with each other are considered in the actual calculation. Moreover, interaction constants referring to the wagging motion of C=O bonds are also neglected because of difficulties in their estimation. Descriptions

will be made of the retained force constants in succession.

Force constants for the torsions around CC bonds are obtained using the relation proposed in a previous paper[4]. Bond orders used were explained above. Overlap integrals used correspond to the CC distances obtained from bond orders. Using these torsional constants interaction constants c_o and $\bar{c}_o$ are obtained using the method which has also been described in a previous paper[4]. Potential constants A, a_o, b_o and b_o' are taken from benzene. The remaining constant A'' is determined in such a way that the calculated value of the lowest B_{3g} fundamental coincides with the smallest Raman shift of 243 cm^{-1} which can be assigned to the B_{3g} mode of lowest frequency, as will be discussed in a subsequent paper[12]. A summary of the value of force constants is given in Table IV.

TABLE IV

VALUES OF FORCE CONSTANTS

(in 10^5 dyn./cm.)

$A''=$ 0.201	$c_o=+0.038$
$A=$ 0.402	$\bar{c}_o=+0.205$
$a_o=-0.073$	$c_o'=$ 0
$a_o'=$ 0	$B=$ 0.048
$b_o'=-0.012$	$B''=$ 0.287
$b_o=-0.011$	

Calculation of the Frequencies and Discussions

Now that all the necessary values of potential constants are determined, it is possible to calculate the frequencies. The calculated values are shown in Table V.

TABLE V

CALCULATED AND OBSERVED FREQUENCIES OF OUT-OF-PLANE VIBRATIONS OF *p*-BENZOQUINONE (cm^{-1})

mode	A_u		B_{1u}		B_{2g}		B_{3g}	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
C=O bending			533	—			(243)	243
C-H bending	962	—	871	876	839	794	959	932
ring bending	403	533	98	99			790	—

In this table experimental frequencies are also given for comparison. All the experimental frequencies, except those belonging to species A_u, are obtained from the analysis of the infrared and Raman data as will be discussed in part IV[12] of this series. Of the two vibrations belonging to species A_u experimental frequency is available only for the lower one (hereafter denoted as $\nu_2(A_u)$) and this frequency is obtained from the vibrational analysis of the electronic spectrum of *p*-benzoquinone vapor.

The agreement between calculated and observed frequencies is fairly good except for $\nu_2(A_u)$. Since the potential constants (both the diagonal and the interaction constants) referring to the wagging of C=O bond do not appear in the **F** matrix for species A_u, the neglect of or the inadequate values of these constants are not the reasons why the calculated $\nu_2(A_u)$ does not agree with the experiment.

In the vibrational analysis of the electronic spectrum lying around 4500 Å to be discussed in a separate article, two bands assigned to vibronic transitions in which $\nu_2(A_u)$ is superimposed by one quantum on the forbidden 0, 0 transition in the ground and the excited state, respectively, are found 1066 cm^{-1} apart from each other. This separation should represent the sum of ground- and excited-state value of $\nu_2(A_u)$. On the other hand it is found in a calculation of the non-planar frequencies for the excited state using the scheme similar to that used for the ground state that $\nu_2(A_u)$ is almost completely insensitive to the electronic excitation concerned. Therefore, one-half of the above-mentioned separation may be considered to represent the value of $\nu_2(A_u)$ in the ground state. Hence, we take 533 cm^{-1} as the "experimental" value of $\nu_2(A_u)$ in the ground state. It is to be noted that the bond angles assumed for the calculation of upper-state frequencies are the same as those used for the ground state, although the change of bond length and torsional force constants are taken into consideration from the bond order. As can been seen in Eq. 20 of reference 4, c_o and $\bar{c}_o$ depend on the bond angles which may be changed by the electronic excitation. Therefore, the reason for the disagreement between calculated and "experimental" values of $\nu_2(A_u)$ should be searched for not only in the calculated but also on the "experimental" side. This point will be discussed more fully in a later paper.

The authors express their sincere thanks to Professor S. Imanishi and to Dr. Y.

12) T. Anno and A. Sadô, This Bulletin, **31**, 734 (1958).

TABLE VI
L MATRIX[a)]

A_u	$\lambda_1(\nu=962\ cm^{-1})$	$\lambda_2(\nu=403\ cm^{-1})$	$\lambda_3(\nu=0\ cm^{-1})$
S_{16a}	1.169 417	2.717 244	0
S_{17a}	3.210 802	1.251 510	0
S_A	−0.049 317	−0.114 592	0

B_{1u}	$\lambda_1(\nu=871\ cm^{-1})$	$\lambda_2(\nu=533\ cm^{-1})$	$\lambda_3(\nu=98\ cm^{-1})$
S_{11}	1.661 739	1.360 246	−0.182 856
S_{16b}	1.602 491	−2.110 660	−0.659 572
S_{17b}	2.543 457	−1.186 288	0.144 455

B_{2g}	$\lambda(\nu=839\ cm^{-1})$
S_{10a}	2.753 927

B_{3g}	$\lambda_1(\nu=959\ cm^{-1})$	$\lambda_2(\nu=790\ cm^{-1})$	$\lambda_3(\nu=243\ cm^{-1})$	$\lambda_4(\nu=0\ cm^{-1})$
S_4	−1.879 766	4.447 465	−0.998 018	0
S_5	2.914 687	−2.090 424	−0.188 288	0
S_{10b}	1.570 902	0.817 234	0.893 017	0
S_G	−0.019 107	0.045 207	−0.010 144	0

a) Numerical values in these tables are based on the length in 10^{-8} cm. and the mass in 10^{-23} gram.

Kanda for their encouragement throughout this work and their kind suggestions in preparing the manuscript.

Appendix: L Matrix

Following Wilson[10] **L** matrix is defined as

$$\mathbf{S} = \mathbf{LQ}$$

where **S** and **Q** are the column matrices formed by the internal (or internal symmetry) and the normal coordinates, respectively. Normalization condition is

$$\mathbf{LL}' = \mathbf{G}$$

in which prime denotes the transpose of the matrix.

Since **L** matrix elements may be used to estimate the change of the frequencies owing to some small changes of the various force constants by the perturbation method[13] we have calculated normalized **L** matrix which is shown in Table VI. Numerical values in this table are based on the length in Å and the mass in 10^{-23} gram.

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13) T. Anno, A. Sadô and I. Matubara, This Bulletin, **29**, 703 (1956).

Electronic States of p-Benzoquinone. IV. Infrared Spectrum and Assignment of Vibrational Frequencies in the Ground Electronic State

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(Received March 31, 1958)

The infrared absorption band due to C=O stretching vibration of the *p*-benzoquinone molecule has been extensively studied by Josien, Fuson et al.[1] together with those of other quinones. Rosenkrantz[2] measured the infrared spectrum of this substance in molten state in 12~2 μ region as one of the basic researches of the analyses of vitamine E and related compounds. Stammreich and Forneris[3] reported the Raman spectrum of *p*-benzoquinone. In spite of these spectroscopic works, however, the assignment of the fundamental frequencies to the modes of vibrations have not yet been reported.

In the present paper the infrared-spectral data of *p*-benzoquinone in carbon disulfide and carbon tetrachloride solutions in rock salt region will be presented and the vibrational analysis will be given utilizing the Raman data of Stammreich and Forneris[3] and the calculated values of the out-of-plane vibrational frequencies reported in a previous paper[4].

Experimental

The sample of *p*-benzoquinone was obtained from a commercial product recrystallizing it several times from ligroin. Solvents used were purified in the usual manner. The infrared spectrum was recorded with Perkin-Elmer model 21 spectrophotometer. The wavelength was calibrated by the spectrum of polystyrene. Wavelengths and relative intensities of observed absorption bands are given in Table I together with Rosenkrantz' data and interpretations discussed below.

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1) M.-L. Josien, N. Fuson, J.-M. Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953); M.-L. Josien and N. Fuson, *Bull. soc. chim. France*, **19**, 389 (1952); *Compt. rend.*, **234**, 1680 (1952); **236**, 1879 (1953); *J. Am. Chem. Soc.*, **73**, 478 (1951); N. Fuson, M.-L. Josien and E. M. Shelton, ibid. **76**, 2526 (1954); M.-L. Josien and J. Deschamps, *J. chim. phys.*, **52**, 213 (1955); **53**, 885 (1956); *Compt. rend.*, **242**, 3067 (1956); A. Hadni, J. Deschamps and M.-L. Josien, ibid. **242**, 1014 (1956).

2) H. Rosenkrantz, *J. Biol. Chem.*, **173**, 439 (1948).

3) H. Stammreich and R. Forneris, *Z. Naturforsch.*, **7a**, 756 (1952).

4) Part III of this series. T. Anno and A. Sadô, This Bulletin, **31**, 728 (1958).

Results and Discussion

Normal Coordinate Treatment of Totally Symmetrical Skeleton Vibrations.—In a later part of this series[5], in which the vibrational analysis of the electronic spectrum will be made, the calculation of the frequencies of the totally symmetrical skeleton vibrations in excited electronic state will be reported. The reason for restricting ourselves to totally symmetrical vibrations is that these are the only vibrations which form the vibrational structure of the electronic spectrum prominently. To compare with this later treatment, ground-state frequencies of the totally symmetrical skeleton vibrations were calculated as described in this subsection. This treatment is expected to help to some extent the vibrational assignment in the ground electronic state.

In this calculation the method proposed by the present authors[6] based on the simple valence force field approximation was used. The stretching force constants of the CC bonds were determined in the same way as in a previous article[6] from the bond order described in another paper[4] assuming the hybridization of carbon σ atomic orbital to be sp^2.

As for CO bond, the force constant was determined from the experimental value of CO distance (r_{CO}) 1.23Å[7] in the following manner since the order-length relation is less well established. In formaldehyde r_{CO}=1.21Å[8] and it is determined that the CO stretching force constant (k_{CO}) is equal to 12.286×10^5 dyn./cm. from the CO stretching frequency of this molecule 1744 cm^{-1} [9] treating the CH_2 group in this

5) Unpublished.

6) T. Anno, A. Sadô and I. Matubara, ibid. **29**, 703 (1956).

7) S. M. Swingle, *J. Am. Chem. Soc.*, **76**, 1409 (1954).

8) R. B. Lawrence and M. W. P. Strandberg, *Phys. Revs.*, **83**, 363 (1951).

9) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York (1945), p. 300.

TABLE I

ABSORPTION BANDS OF *p*-BENZOQUINONE IN THE INFRARED REGION TOGETHER WITH INTERPRETATION (cm^{-1})

CS_2 solution	CCl_4 solution	Crystalline melt[a]	Interpretation
3322 mw[b]	3333 mw		$1667+1667=3334$ (B_{2u})
3268 mw	3279 mw		$3049+243=3292$ (B_{1u})
3049 w	3049 w	3058 s	$b_{2u}+b_{3u}$ fundamentals
2681 vw			
2577 vw			$876+1688=2564$ (B_{1u})
2445 vw			$1298+1149=2447$ (B_{2u})
1968 w	1976 w	2008 vw	
1869 w	1880 w	1908 vw	$1064+794=1858$ (B_{1u})
1764 m	1767 m	1761 vw	$99+1667=1766$ (B_{1u})
1715 ms	1721 ms		b_{2u} fundamental
1667 vs	1675 vs		$1064+610=1674$ (B_{2u})
1656 vs	1664 vs	1664 s	b_{2u} fundamental
	1597 ms	1595 s	$1064+540=1604$ (B_{2u})
1355 m	1357 m		b_{3u} fundamental
1323 m	1323 m	1337 s	$876+444=1320$ (B_{1u})
1297 vs	1300 vs	1302 vs	b_{2u} fundamental
1174 vw	1171 w		$730+444=1174$ (B_{2u})
1139 w	1139 w	1135 w	$370+770=1140$ (B_{3u})
1116 vw	1119 w		$876+243=1119$ (B_{2u})
1063 vs, b	1065 vs	1079 m	b_{3u} fundamental
983 mw		1001 w	$370+610=980$ (B_{2u}) $730+243=973$ (B_{1u})
943 s	945 s	949 s	b_{3u} fundamental
876 vs	883 vs	909 m	b_{1u} fundamental
730 mw, b			b_{2u} fundamental

a) Estimated from absorption curve given in Ref. 2.
b) Abbreviations denoting relative intensities are as follows: vs=very strong, s=strong, ms=medium strong, m=medium, mw=medium weak, w=weak, vw=very weak, b=broad.

molecule as a mass point. Since in Badger's relation[10]

$$r_{CO}=(C/k_{CO})^{1/3}+d_{CO},$$

C is considered to be a universal constant and $C^{1/3}=1.230$[6,10], d_{CO} can be determined from the r_{CO} and k_{CO} values for formaldehyde described above. Then it follows that $d_{CO}=0.677$ Å, which is in good agreement to the value given by Badger[10a]. From the d_{CO} value thus obtained and the experimental value of r_{CO} (1.23 Å) k_{CO} for *p*-benzoquinone is calculated to be 11.004×10^5 dyn./cm. As will be discussed later, it seems to be most appropriate to assign the Raman line reported as 444cm^{-1} to the ring-defomation vibration belonging to a_g. This frequency was used to evaluate the ring-deformation force constant. From these values of force constants the totally symmetrical vibrational frequencies shown in Table II are obtained.

10) (a) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934). (b) R. M. Badger, ibid., **3**, 710 (1935).

TABLE II

CALCULATED FREQUENCIES OF TOTALLY SYMMETRICAL SKELETON VIBRATIONS OF *p*-BENZOQUINONE (cm^{-1})

(444)[a]
782
1596
1900

a) The value in parentheses is used to calculate the ring deformation force constant.

Assignment of Fundamental Frequencies.—In this subsection the assignment of the fundamental frequencies will be discussed using the Raman and infrared spectral data as well as the calculated values of frequencies. Group-theoretical considerations for the normal vibrations of *p*-benzoquinone were briefly given in a previous paper[4] and will not be repeated here. As to the planar vibrations the calculation of the frequencies is made only for the totally symmetrical skeleton vibrations, so the comparison with the

TABLE III

COMPARISON OF FUNDAMENTAL FREQUENCIES OF IN-PLANE MODES OF VIBRATION IN MOLECULES OF TYPE X-⬡-X[a]

(Frequencies are given in the unit of cm^{-1})

Modes	Species a_g			Species b_{1g}			Species b_{2u}			Species b_{3u}		
	X=D[b]	F[c]	O	D[b]	F[c]	O	D[b]	F[c]	O	D[b]	F[c]	O
CH stretching	3050(ν_{7a})	3048	3058	3042(ν_{7b})	3080	3058	3060(ν_{13})	3028	3049	3079(ν_{20b})	3088	3049
CX stretching	2280(ν_2)	1245	1667				2275(ν_{20a})	1183	1667			
CC stretching	1587(ν_{8a})	1617	1688	1569(ν_{8b})	1285	610	1469(ν_{19a})	1511	1715	1603(ν_3)	1437	943
CC breathing	978(ν_1)	859	770				992(ν_{12})	737	730	1413(ν_4)	1212	1063
CX bending				909(ν_{9b})	635 [~400]					814(ν_{18b})	350	370
CH bending	1173(ν_{9a})	840	1149	1309(ν_3)	1142	1360	1033(ν_{18a})	1012	1297	1106(ν_{15})	1085	1355
ring bending	597(ν_{6a})	451	444	601(ν_{6b})	507	540						

a) X=D, F and O for *p*-dideuterobenzene, *p*-difluorobenzene and *p*-benzoquinone, respectively.
b) Frequencies taken from Garforth, Ingold and Poole (*J. Chem. Soc.* **1948**, 406) are followed by Wilson's numbering scheme (*Phys. Revs.*, **45**, 706 (1934)).
c) E. E. Ferguson, R. L. Hudson, J. R. Nielsen and D. C. Smith, *J. Chem. Phys.*, **21**, 1457 (1953).

spectral data of similar molecules may be helpful. The data used for comparison are those of *p*-dideuterobenzene[11] and *p*-difluorobenzene[12]. These are listed in Table III together with the assignment to the mode of vibrations.

Raman-active Frequencies.—*Species* a_g. —Although of the Raman-active frequencies those belonging to species a_g give polarized Raman lines, the depolarization factors of the Raman lines of *p*-benzoquinone have not been studied yet. However, it is known that the totally symmetrical vibrations produce, in general, stronger Raman lines in comparison with the other types of vibrations. It will be natural to assign the Raman lines at 3058 cm^{-1} and 1667 cm^{-1} to CH and CO stretching vibrations belonging to a_g, respectively, from the intensities and the magnitudes of so-called group frequencies[13]. The ring bending vibration belonging to a_g in this molecule corresponds to 606 cm^{-1} benzene value. As can be seen in Table III the corresponding frequency in *p*-benzoquinone should be sought around 450 cm^{-1}. It is reporteted that the Raman line at 444 cm^{-1} is a relatively stronger one in its neighborhood[3]. Moreover, in the normal-coordinate treatment of totally symmetrical skeleton vibrational frequencies described above a fairly large change of the ring deformation force constant results, if we change the value of the frequency to be inserted for the determination of this constant a little in the neighborhood of 444 cm^{-1}. These facts suggest that 444 cm^{-1} may be assigned to the a_g ring-bending vibration. As described previously if the ring-bending force constant is determined from this frequency, the calculated values of totally symmetrical skeleton vibrational frequencies shown in Table II are obtained. Of these values the calculated value of 1900 cm^{-1} which may correspond to the experimental value of 1667 cm^{-1} agree with the experiment only poorly. This may be due either to the experimental error of CO bond length or to the fact that the bond length-force constant relation has not been established well. Moreover, from the calculation of **L**-matrix elements[14] it can be shown that this frequency is fairly sensitive to the interaction constants, so use of valence-force field approximation may not be adequate for the calculation of this frequency. On the other hand, since the order-length and the length-force constant relations are established fairly well for CC bonds, it is expected that the agreement between the calculated values and the experimental ones is fairly good for CC breathing and stretching vibrations. Therefore, 770 and 1688 cm^{-1} Raman lines may be assigned to CC breathing and stretching vibrations belonging to a_g from comparison with the calculated values. The remaining vibration belonging to this species is an in-plane bending vibration of the hydrogen atom and is expected to

11) F. M. Garforth, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, **1948**, 406.
12) E. E. Ferguson, R. L. Hudson, J. R. Nielsen and D. C. Smith, *J. Chem. Phys.*, **21**, 1457 (1953).
13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen and Co., Ltd., London (1954).
14) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941). See also the last section of Ref. 6.

TABLE IV

FUNDAMENTAL FREQUENCIES OF *p*-BENZOQUINONE (GROUND ELECTRONIC STATE) (cm^{-1})[a, b]

	a_g	b_{1g}	b_{2g}	b_{3g}	a_u	b_{1u}	b_{2u}	b_{3u}
C—H stretching	3058	3058					3049	3049
C=O stretching	1667						1667	
C—C stretching	1688	610					1715	944
C—C breathing	770						730	1064
C=O bending		[~400][c]		243 (—)		—(533)		370
C—H bending	1149	1360	794(839)	932(959)	—(962)	876(871)	1298	1356
ring bending	444	540		—(790)	533(403)	99 (98)		

a) Calculated values of non-planar vibrational frequencies are closed in parentheses.
b) Experimental values with underlining are obtained from combination bands or electronic spectral data (see text).
c) Estimated.

appear in the region of 1100~1300 cm^{-1}. From its intensity the Raman line at 1149 cm^{-1} may be assigned to a_g. Therefore it is natural to assign this frequency to the CH in-plane bending vibration belonging to a_g.

Species b_{2g} and b_{3g}.—Before discussing the Raman-active in-plane mode other than those belonging to species a_g the Raman-active out-of-plane species b_{2g} and b_{3g} will be discussed.

Of the C=O out-of-plane bending vibrations the one which is symmetric with respect to inversion belongs to b_{3g}. Although the out-of-plane deviations of the oxygen atom from the molecular plane decreases the overlap of the σ AO of the oxygen atom with the σ AO of the carbon atom to which the oxygen atom in question is attached, the increase of the potential energy thus results will be partially compensated by the increase in the overlap of π AO of the oxygen atom with σ AO of the carbon atom. Compensation of such a kind in the potential energy is not expected in the case of C=O in-plane bending mode. Therefore it is expected that C=O out-of-plane bending frequency is rather low and lower than that of C=O in-plane bending. The Raman line reported at 243 cm^{-1} may represent this vibration. This is the Raman line of lowest frequency reported by Stammreich and Forneris[3] and the Raman line of lowest frequency is assigned to species b_{3g} (in our notation) also in the case of *p*-difluorobenzene[12].

As described in a previous paper[4] if 243 cm^{-1} is used as the b_{3g} C=O out-of-plane bending vibrational frequency in order to determine the force constant of C=O out-of-plane bending motion, the other nonplanar vibrational frequencies of *p*-benzoquinone shown in parentheses in Table IV are obtained. From the comparison with these calculated values Raman lines at 794 and 932 cm^{-1} are assigned to b_{2g} and b_{3g} fundamentals, respectively. The remaining calculated frequency belonging to species b_{3g} is 790 cm^{-1} and has no corresponding Raman line.

Species b_{1g}.—One of the five b_{1g} fundamentals is a hydrogen stretching mode which is assumed to overlap the Raman line at 3058 cm^{-1} assigned to a_g. Raman lines at 540, 610 and 1360 cm^{-1} which have been left unassigned may all be assigned to the b_{1g} fundamentals. The last frequency may be assigned to an in-plane hydrogen bending vibration with considerable certainty, while the other two may be caused by carbon vibrations. It is true that one of the C=O in-plane bending modes is contained in this species and 540 or 610 cm^{-1} Raman line might be assigned to this vibration. However, the C=O in-plane bending frequency belonging to species b_{1g} is expected to lie around 400 cm^{-1} from comparison with the data of *p*-difluorobenzene (see Table III) and with the frequency of another C=O in-plane bending vibration belonging to species b_{3u} of *p*-benzoquinone. Therefore we believe that none of the three Raman frequencies mentioned above correspond to this vibration and there fails the Raman line corresponding to this vibration. We assign 540 cm^{-1} to ring bending mode and 610 cm^{-1} to C—C (single bond) stretching mode. This assignment for 540 cm^{-1} is also consistent with the fact, which may be seen in Table III, that b_{1g} component of 606 cm^{-1} e_g^+ benzene vibration diminishes in frequency only slightly although the a_g component is lowered considerably.

Infrared-active Frequencies.—*Species b_{2u}.*—Infrared bands at 3049 cm^{-1} and 1667 cm^{-1}

may be assigned to two of the five b_{2u} fundamental vibrations, namely the hydrogen and oxygen stretching vibrations, with considerable certainty by comparison with the values of the corresponding symmetric (a_g) vibration. We note here that the double maximum of the latter band (1667 and 1656 cm^{-1} in carbon disulfide) is interpreted to be caused by Fermi resonance between the b_{2u} fundamental and $1064(b_{3u})+610(b_{1g})=1674(B_{2u})cm^{-1}$ combination as shown in Table I. A medium strong band at 1715 cm^{-1}, which can not be explained as a combination, may represent CC stretching vibration. This assignment is consistent with the corresponding values of the frequencies in *p*-dideuterobenzene and *p*-difluorobenzene as shown in Table III. A medium weak and broad band at 730 cm^{-1} may be assigned to the ring-breathing vibration from comparison with the corresponding vibrations in other molecules (see Table III). The remaining vibration of this species is the hydrogen bending vibration. It must be searched for in the region between 1100 and 1400 cm^{-1} from the values of the corresponding Raman-active mode. They must be selected among medium to very strong bands observed at 1355, 1323 and 1297 cm^{-1}, of which the middle one can also be explained as a combination band as shown in Table I. We assign the remaining bands to hydrogen bending vibration, 1355 cm^{-1} and 1297 cm^{-1} being taken as b_{3u} and b_{2u} fundamentals, respectively. It is to be noted that the following sequence results for frequency values of hydrogen bending vibration from this assignment together with the assignment of the Raman-active fundamentals described previously: $b_{1g}>b_{3u}>b_{2u}>a_g$. This sequence also exists in the case of *p*-difluorobenzene[12].

Species b_{3u}.—One of the five b_{3u} fundamental vibrations is the hydrogen stretching mode which is assumed to overlap the band at 3049 cm^{-1} assigned to a b_{2u} fundamental. Mention was made of another fundamental, i. e., the hydrogen bending vibration, which was taken to be 1355 cm^{-1}. Strong or very strong bands at 943 and 1063 cm^{-1} may also be taken as b_{3u} fundamentals. The remaining fundamental vibration is an oxygen in-plane bending mode and this is expected to have a frequency of 400 cm^{-1} from the comparison with the corresponding vibrational frequency of *p*-difluorobenzene. Although this region is outside our measurements, we tentatively assign the value of 370 cm^{-1} to this vibration because this assumption favors the explanation of some of the absorption bands as combinations.

Species b_{1u}—Calculated values of three non-planar frequencies belonging to this species are 98, 533 and 871 cm^{-1}. The highest frequency is realized in the spectrum by the band at 876 cm^{-1}. Although we could not obtain the experimental value of frequency corresponding to the calculated value of 533 cm^{-1} even from the combination bands, we infer the experimental value of the lowest b_{1u} fundamental to be 99 cm^{-1} from the combination band (see Table I).

Inactive Frequencies.—*Species* a_u.—The two vibrations in species a_u are neither active in the Raman nor in the infrared spectra. Calculated values of these vibrational frequencies are 403 and 962 cm^{-1}. Although we infer the "experimental" value corresponding to the former frequency to be 533 cm^{-1} from the vibrational analysis of the electronic spectrum, this value should be considered to be tentative for reasons described briefly in a previous paper[4].

TABLE V
INTERPRETATION OF RAMAN SPECTRUM OF *p*-BENZOQUINONE

$\Delta\nu$ (cm^{-1})[3]	Interpretation
243 (3)	b_{3g} fundamental
444 (4)	a_g fundamental
540 (2)	b_{1g} fundamental
610 (3)	b_{1g} fundamental
770 (2)	a_g fundamental
794 (1)	b_{2g} fundamental
932 (2)	b_{3g} fundamental
1149 (7)	a_g fundamental
1360 (3)	b_{1g} fundamental
1667 (10)	a_g fundamental
1688 (5?)	a_g fundamental
3058 (4)	a_g+b_{1g} fundamentals

Interpretation of Spectra. — Fundamental frequencies assigned are summarized in Table IV. The interpretations of the Raman and infrared spectra are included in Tables V and I, respectively. In interpreting the bands as combinations only the possibilities of binary combinations were considered. In Table IV, underlined values were obtained from the combination bands (lower a_u fundamental was obtained from the electronic spectral data — see above) and the calculated values of non-planar frequencies are given in parentheses. The value of frequency

of C=O bending vibration belonging to species b_{1g} is only an estimated value and is included in brackets.

Summary

The infrared absorption spectra of *p*-benzoquinone in carbon disulfide and carbon tetrachloride solutions in rock salt region are measured and interpreted together with the Raman data reported by Stammreich and Forneris[3]. A complete, although more or less tentative, assignment of the fundamental frequencies to modes of vibrations is proposed.

The authors express their sincere thanks to Professor S. Imanishi and to Dr. Y. Kanda for their encouragement throughout this work and their kind suggestions in preparing the manuscript. Thanks are also due to the Research Department of Toyo Rayon Co., Ltd. for recording infrared spectrum.

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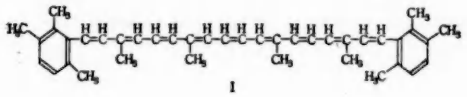
*Renieratene, a New Carotenoid Containing Benzene Rings, Isolated from a Sea Sponge**

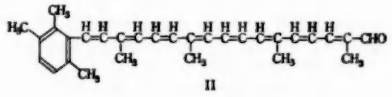
By Masaru YAMAGUCHI

(Received March 5, 1958)

With regard to the chemical constitution of renieratene[1], a carotenoid pigment isolated from a sponge "*Reniera japonica*", it has previously been shown from the result of the chromic acid oxidation, by which crocetin dialdehyde has been isolated besides other products, that renieratene is a derivative of tetramethyl-octadeca-nonaene[2]. Shortly afterwards the author has elucidated the chemical constitution of isorenieratene (I), and it has become clear that isorenieral which is the degradation product of the former, has the constitution indicated by II[3]. As isorenieral is also one of the degradation products of renieratene, it is clear that renieratene can be expressed by the partial formula III. Therefore the remaining problem in the chemical constitution of renieratene is the elucidation of R-group in the formula III. From the molecular formula of renieratene, $C_{40}H_{48}$, and the number of double bonds, 15, it can be concluded that the R-group has the formula C_9H_{11}–, and that it contains one ring and three double bonds. Furthermore, it can be inferred from the analogy with another terminal group, that the ring may be a benzene ring.



I



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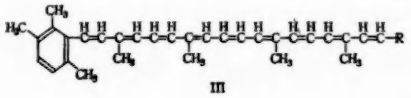


III

In the present paper is described the potassium permanganate oxidation of renieratene, by which whole its constitution has been clarified.

The oxidation products were separated into some neutral and acidic fractions by the ordinary method. From the neutral

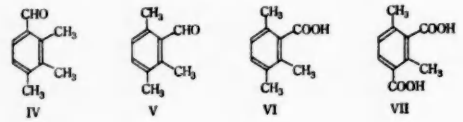
* "Pigments of Marine Animals", VI. V of this series, This Bulletin, **31**, 51 (1958).

1) T. Tsumaki, M. Yamaguchi and T. Tsumaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 297 (1954); M. Yamaguchi, This Bulletin, **30**, 111 (1957).

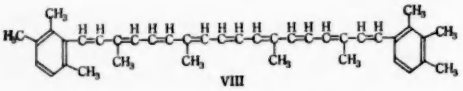
2) M. Yamaguchi, ibid., **30**, 979 (1957).

3) M. Yamaguchi, ibid., **31**, 51 (1958).

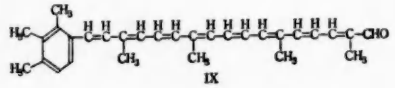
fractions a considerable amount of 2,3,4-trimethylbenzaldehyde (IV) was obtained in the form of semicarbazone. The confirmation was done by the mixed melting point determinations of the semicarbazone and 2,4-dinitrophenylhydrazone with the authentic samples and further by the oxidation into 1,2,3,4-benzene-tetracarboxylic acid. As another neutral constituent, 2,3,6-trimethylbenzaldehyde (V) which was fairly reasonably expected, was obtained in the form of 2,4-dinitrophenylhydrazone by the chromatographic separation, from the mother liquor of the above semicarbazone. From the petroleum ether soluble part of the acidic fraction, a small quantity of 2,3,6-trimethylbenzoic acid (VI) was isolated in the form of its 4-phenylazophenacyl ester. However the main part of the acidic fraction consisted of an acid of m. p. 205~220°, which gave 1,2,3,4-benzene-tetracarboxylic acid, on oxidation. As the acid of m. p. 205~220° could not be purified effectively by recrystallization, it was converted into 4-phenylazophenacyl ester. The main product thus obtained after the chromatographic separation was a di-ester of 2,4-dimethyl-benzene-1,3-dicarboxylic acid (VII).



IV V VI VII



VIII



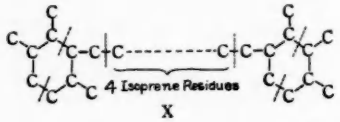
IX

These results decidedly show that besides 2,3,6-trimethylphenyl group as one terminal group, 2,3,4-trimethylphenyl group must exist as another terminal group which has been expressed by R-group in III. Therefore the structural formula of renieratene can be given by VIII. This formula can explain all its properties or behaviors hitherto observed[1,2].

Renieral, which, as well as isorenieral, is a degradation product of the mild oxidation of renieratene[2], can therefore be considered to have a 2,3,4-trimethylphenyl group, and can be expressed by the formula IX.

It has already been pointed out that for the explanation of the spectral properties of isorenieratene, it is necessary to suppose the steric hindrance caused by the two methyl groups which are standing at the two neighboring positions of the polyene chain in benzene ring[3]. In the case of renieratene, the position of the absorption maxima can also be accounted for by the same effect. The difference between the wavelength of the longest wavelength maximum of diphenyltetramethyl-octadeca-nonaene[4], 541 mμ in carbon disulfide, and that of isorenieratene, 520 mμ in the same solvent, is ca. 21 mμ. The effect caused by only one 2,3,6-trimethylphenyl group can therefore be considered to be a half, i.e. about 10 mμ. Renieratene has one 2,3,6-trimethylphenyl group and one 2,3,4-trimethylphenyl group. As the latter possesses only one methyl group at the *o*-position to the polyene chain, the steric effect may be much smaller than that caused by the former. Therefore renieratene will possess the longest wavelength maximum at ca. 10 mμ shorter wavelength position than that of unsubstituted diphenyltetramethyl-octadecanonaene, i.e. at 531 mμ. This value shows good agreement with the observed value, 532 mμ, of renieratene.

Renieratene can be considered to be resolved into isoprene unites. However, as indicated in X, the modes of binding of isoprene residues in the terminal groups of renieratene are considerably different from those in the carotenoids of plant-occurence, in which isoprene residues are arranged top-to-tail. Therefore, in these respect also, renieratene can be regarded as a carotenoid of a new type.



X

Experimental

Renieratene (200 mg.) dissolved in pure benzene (90 cc.) and potassium permanganate (2.7 g.) and sodium carbonate (2.7 g.) dissolved in water (100 cc.) were stirred efficiently at the room temperature. After 8 hours the color of the benzene layer completely disappeared. The excess of permanganate was reduced with the solution of sodium hydrogen sulfite, the precipitates were

4) C. H. Eugster, C. Garbers and P. Karrer, *Helv. Chim. Acta*, **35**, 1179 (1952).

filtered and washed several times with hot benzene and water. The filtrate and washings were combined and treated as below.

2,3,4-Trimethylbenzaldehyde.—The benzene layer of the above product was separated, washed with water, dried with sodium sulfate, and concentrated under diminished pressure. The oily residue was dissolved in ethanol (10 cc.) and treated with the solution of semicarbazide hydrochloride (40 mg.) and sodium acetate (80 mg.) in water (2 cc.). After 24 hours the precipitates were collected, and the recrystallization from ethanol gave 2, 3, 4-trimethylbenzaldehyde semicarbazone in colorless plates, m. p. 240~242°, (16 mg.).

Anal. Found: C, 64.47; H, 7.43. Calcd. for $C_{11}H_{15}ON_3$: C, 64.36; H, 7.37%.

The semicarbazone (7 mg.), potassium permanganate (45 mg.) and sodium carbonate (45 mg.) were mixed and finely ground, and after the addition of water (3 cc.) heated on the steam bath for 12 hours with occasional additions of a small amount of potassium permanganate. The precipitates were dissolved by the addition of sodium hydrogen sulfite solution and diluted sulfuric acid, and the solution was extracted many times with ether. Ether was evaporated and the residue, recrystallized from water, yielded 1, 2, 3, 4-benzene-tetracarboxylic acid in colorless plates (2 mg.), m. p. 215~236°, which was identified by the light absorption curve and mixed melting point determination with the authentic sample.

The semicarbazone gave 2,4-dinitrophenylhydrazone in red needles, m. p. 227~229°, when treated with 2, 4-dinitrophenylhydrazine in ethanolic sulfuric acid. The semicarbazone and the hydrazone exhibited no melting point depression when mixed with the authentic samples derived from the synthetic 2, 3, 4-trimethylbenzaldehyde. (It was synthesized from 4-bromohemimellithene and ethyl orthoformate by Grignard reaction[5]). Semicarbazone, colorless plates from ethanol, m. p. 240~242°. *Anal.* Found: C, 64.28; H, 7.21. Calcd. for $C_{11}H_{15}ON_3$: C, 64.36; H, 7.37%. 2, 4-dinitrophenylhydrazone, red needles from benzene-ethanol, m. p. 229°. *Anal.* Found: C, 58.77; H, 5.09. Calcd. for $C_{16}H_{16}O_4N_4$: C. 58.53; H, 4.91%.)

2,3,6-Trimethylbenzaldehyde.—The mother liquor of the above semicarbazone was treated with 2, 4-dinitrophenylhydrazine and sulfuric acid in ethanol. The precipitates (31 mg.) were recrystallized from benzene-ethanol and adsorbed on alumina (column, 2×15 cm.; developer, benzene), forming two main zones. The upper brown zone gave red needles of 2, 3, 4-trimethylbenzaldehyde-2', 4'-dinitrophenylhydrazone (11 mg.), m. p. 225~228°, when recrystallized from benzene-ethanol.

Anal. Found: C, 58.62; H, 5.18. Calcd. for $C_{16}H_{16}O_4N_4$: C, 58.53; H, 4.91%.

5) The aldehyde has been reported to be synthesized from hemimellithene by Gattermann-Koch's reaction, but no characterizations has been described. H. A. Smith and J. A. Stanfield, *J. Am. Chem. Soc.*, **71**, 81 (1949).

The lower orange zone afforded 2, 3, 6-trimethyl benzaldehyde-2', 4'-dinitrophenylhydrazone in red needles (13 mg.), m. p. 219°.

Anal. Found: C, 58.88; H, 4.94. Calcd. for $C_{16}H_{16}O_4N_4$: C, 58.53; H, 4.91%.

2,3,6-Trimethylbenzoic Acid.—The aqueous solution separated from benzene layer containing neutral fractions was concentrated under vaccum to ca. 4 cc., acidified with sulfuric acid (20%), and extracted with ether (total, 50 cc.). Ether was evaporated and the residue was extracted with petroleum ether (3 cc.). The petroleum ether solution was evaporated and the oily residue was neutralized with the solution of sodium hydroxide (20.6 cc., 0.0143 N) using phenolphthalein. The indicator was removed by the ether extraction, the solution was evaporated to dryness and the residue was heated under reflux with 4-phenylazophenacyl bromide[6] (80 mg.) in ethanol (3 cc.) for 30 minutes. The product was dissolved in benzene (10 cc.), washed with water, dried, and chromatographed on alumina (column, 2×20 cm.; developer, benzene) giving seven zones. The third orange zone from the top afforded faint red needles (ca. 1 mg.), m. p. 165~169°, when recrystallized from benzene-ethanol. It seemed to be an impure ester of 2, 4-dimethylbenzene-1, 3-dicarboxylic acid described below. The sixth orange zone afforded red needles of 4'-phenylazophenacyl-2, 3, 6-trimethylbenzoate (2.3 mg.), m. p., 160~162°, when the residue of the eluate was recrystallized twice from benzene-ethanol. Mixed m. p. 160~162°.

Anal. Found: N, 7.28. Calcd. for $C_{24}H_{22}O_3N_2$: N, 7.25%.

2,4-Dimethylbenzene-1,3-dicarboxylic Acid.—The colorless residue of the above petroleum benzine extraction was recrystallized from water giving colorless solid (12 mg.), m. p. 205~220°. As it was unsuccessful to obtain pure substance by recrystallization, a part of the sample (5 mg.) was oxidized with potassium permanganate (35 mg.) and sodium carbonate (35 mg.) in a way as described in the oxidation of semicarbazone, yielding a small quantity of 1, 2, 3, 4-benzene-tetracarboxylic acid in colorless plates, m. p. 215~230°, mixed m. p. 215~230°.

The remaining part (ca. 6 mg.) was neutralized with a sodium hydroxide solution and after the removal of the indicator the solution was evaporated. The residue was refluxed with 4-phenylazophenacyl bromide (20 mg.) in ethanol (3 cc.) for one hour. When chromatographed on alumina (column, 2×15 cm.; solvent, benzene) the precipitates gave a main orange zone besides several minor zones. The main zone was eluted with benzene containing methanol and the residue of the eluate was recrystallized from benzene-ethanol, yielding di-(4'-phenylazophenacyl)-2, 4-dimethylbenzene-1,3-dicarboxylate in fine red needles (5 mg.), m. p. 169~172°.

Anal. Found: C, 71.15; H, 4.75. Calcd. for $C_{38}H_{30}O_6N_4$: C, 71.46; H, 4.74%.

6) S. Masuyama, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **71**, 402 (1950).

The ester exhibited no melting point depression when mixed with the authentic sample (prepared from synthetic acid[8]; red needles, m. p. 172°. *Anal*: C, 71.12; H, 4.83%.).

The author wishes to express his thanks to Professor Tokuichi Tsumaki for his exceedingly kind directions throughout this work. The author also thanks Mr. Michio Shido and Miss Sachiko Indo for microanalysis. The cost of this work has been partially covered by the Scientific Research Grant of Ministry of Education.

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Relations between the Substructure and the Rate of the Sluggish Inversion of Quartz Rock

By Taneki TOKUDA

(Received March 31, 1958)

Rate of the Sluggish Inversion from Quartz to Cristobalite. — We have confirmed the fact that all of these quartz specimens were slowly converted into cristobalite when heated at 1000~1600°C in air, carbon monoxide, or steam. Tridymite has never been detected by X-ray diffraction. The rate of the sluggish inversion from quartz to cristobalite was calculated from density measurement using the following formula,

$$X = D_2(D_1 - D)/D(D_1 - D_2)$$

where X is the fraction converted, D is the apparent density at a given time of firing, D_1 is the apparent density of quartz aggregates, D_2 is the apparent density of cristobalite aggregates (D_1 and D_2 was corrected for irreversible expansion of polycrystal aggregates[1]). It was found that this sluggish inversion is a reaction of the first order although the rates are found to be different for air, steam, or for such a reducing atmosphere as carbon monoxide. The results obtained when heated in air are shown in Fig. 1. Chemical analysis of the quartz rock specimens is shown in Table I.

These specimens are divided into three classes as can be seen in this figure; a) pegmatite quartz, b) recrystallized cherty part or interstitial quartz veinlet part in

TABLE I
CHEMICAL ANALYSIS OF QUARTZ SPECIMENS

Sample No.	3	5	6	9	10	12
Classification	Unmetamorphosed (Radiolarian) red chert	Slightly metamorphosed red chert	Recrystallized part in red-white silica stone	Vein quartz in red-white silica stone	Vien quartz in green-white silica stone	Pegmatite quartz
Locality	Kuroda	Tamba	Tamba	Tamba	Wakasa	Hongū
SiO_2	94.12	95.68	97.23	99.13	99.40	99.72
Al_2O_3	1.87	2.87	0.20	0.01	0.12	0.00
Total iron as Fe_2O_3	1.89		2.12	0.63	0.15	0.14
CaO	0.25	0.81	0.09	0.09	trace	0.10
MgO	0.66	0.24	0.03	0.01	—	0.00
MnO	0.24	—	—	—	—	—
Alkalis	—	—	0.18	0.11	0.10	—
Ig. loss	0.77	0.19	0.09	0.10	0.05	0.00
Total	99.80	99.79	99.99	100.08	99.82	99.96

1) T. Tokuda, This Bulletin, **28**, 435 (1955).

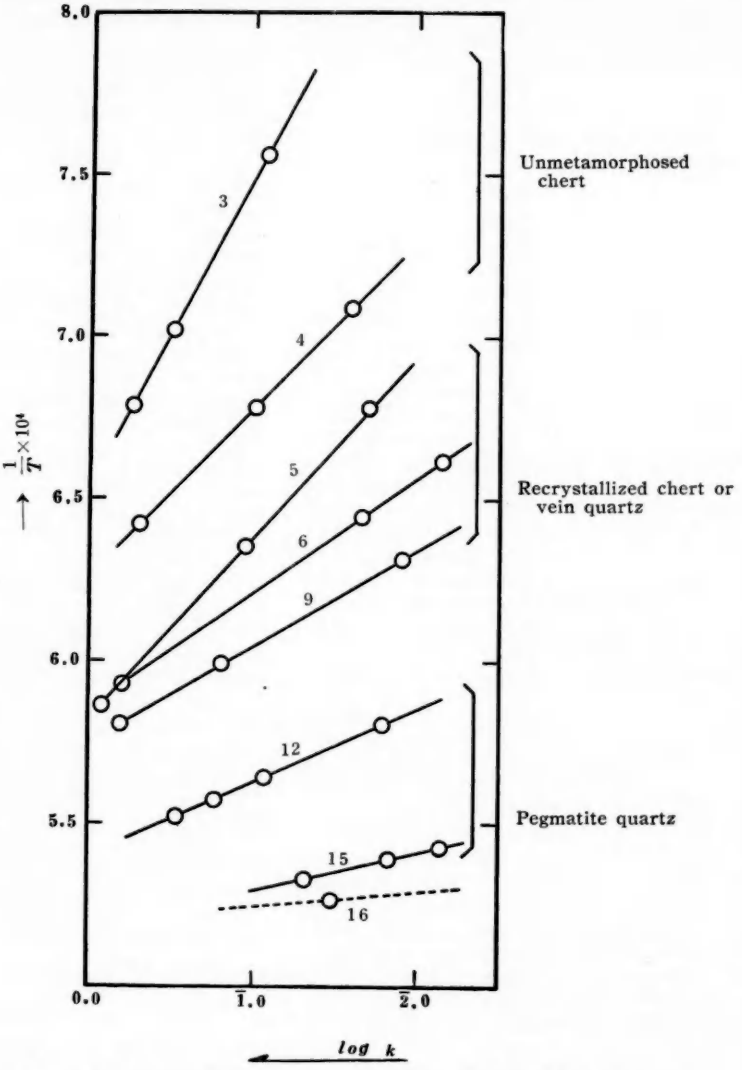

Fig. 1. The rate of the sluggish inversion of several specimens of natural quartz in Japan from quartz to cristobalite (This inversion was a reaction of first order, and k(hr.$^{-1}$) is a rate constant) when heated at a constant temperature (T°K) in an electric furnace. The heating atmosphere was the air. Numbers (1—14) on lines indicate the sample numbers in Table III.

silica stone and c) unmetamorphosed or slightly metamorphosed chert. Quartz occurring as veinlets in the green-white silica stone or red-white silica stone belongs to the same group as recrystallized chert, but not to the pegmatite quartz group.

Variation of Line Breadths.—In order to compare the imperfection of quartz crystals of contrasted geologic origin, the width at half maximum of lines $(234)\alpha_1$, and $(240)\alpha_1$ was determined by means of "Norelco" X-ray diffractometer. Filtered copper K-rays were used with the X-ray tube running at 35 kV., 10 mA. The scanning speed of the GM-counter was 1/8° per minute. Operation condition of the rate

meter was, scale factor 4, multiplier 1, and time constant 16 sec. Divergence and scatter slits were 4°, and receiving slit was 0.006 (inches).

TABLE II
GRAIN SIZE OF QUARTZ SPECIMENS VS. INTENSITY AND WIDTH AT HALF MAXIMUM

	Intensity (cps)	width at half maximum (Degree)
<400 mesh	75.0	0.505
<200 mesh	75.6	0.500

Grain size effect was checked with vein quartz specimens (Table II). As shown in the table, the difference of line breadth and intensity obtained from two specimens, the one ground to pass a 200-mesh, screen and the other ground to pass a 400-mesh, was smaller than 1%. Therefore, in the following, all the measurements were made with samples which were ground to pass a 200-mesh screen. The results obtained for $(234)\alpha_1$ are shown in Table III. Those specimens of quartz which contain more impurities and smaller activation energy of sluggish inversion, have larger line breadth.

Lattice Spacing Variation.— Variation of the spacings of quartz specimens has been measured in the back reflection region. Relative values of the spacings (234) and (240) have been determined by mixing silicon powder with the quartz specimens, and measuring the relative positions of the $(642)\beta_1$ reflection of the silicon and the $(240)\alpha_1$ reflection of quartz. The 2θ value of the $(642)\beta_1$ reflection was taken as 147.152° (at 20°C). Results obtained are shown in Table III. As is shown in this table, those quartz specimens which contain more impurities and smaller activation energy of the sluggish inversion, have larger spacings.

These results, obtained by the measurement of variation of line breadth and lattice spacings, suggest that the impurities might be included in the quartz matrix forming a solid solution. Lattice distortion due to the formation of solid solution would be one of the causes which lower the activation energy of the sluggish inversion.

Conclusion

1) The sluggish inversion of quartz rock of different origins, from quartz to cristobalite, was the primary reaction

TABLE III
WIDTH AT HALF MAXIMUM AND SPACING OF $(234)\alpha_1$ (AT 20°C) VS. ACTIVATION ENERGY OF SLUGGISH INVERSION FROM QUARTZ TO CRISTOBALITE (CuK_{α_1}=1.540501 Å)

No.	Classification of quartz specimens	Locality	Silica content (%)	Line breadth (Degree)	D (Å)	Diffraction angle (2θ) (Degree)	Spacings (Å)	Energy of activation (kcal.)
1	Siliceous shale	Kamiiso, Japan	—	1.5	230	153.16	0.792	—
2	Hot spring product	Onikōbe, 〃	—	0.8	620	153.17	0.792	—
3	Unmetamorphosed (Radiolarian) red chert	Kuroda, 〃	94.12	0.8	620	153.53	0.79125	48
4	Unmetamorphosed (Radiolarian) grey chert	Kyōto 〃	94.42	0.700	760	153.54	0.79124	88
5	Slightly metamorphosed red chert	Tamba, 〃	95.68	0.650	910	153.55	0.79123	81
6	Recrystallized red chert (Chert part of a breccia)	〃 〃	97.23	0.530	1220	153.57	0.79120	120
7	Recrystallized white chert and vein (A breccia)	Ofuku, 〃	—	0.525	1250	—	—	—
8	Quartzite	Hwang He Do, Korea	—	0.515	1290	153.57	0.79120	—
9	Vein quartz (Vein part of a breccia)	Tamba, Japan	99.13	0.500	1340	153.57	0.79120	145
10	Vein quartz (Vein part of a breccia)	Wakasa, 〃	—	0.455	1670	—	—	—
11	Quartzite	Okuyama, 〃	—	0.447_5	1730	—	—	—
12	Pegmatite quartz	Hongū, 〃	99.72	0.427_5	1930	153.58	0.79119	205
13	Quartzite	Yakeyama, 〃	—	0.412_5	2110	—	—	—
14	〃	Yagen, 〃	—	0.410	2140	—	—	—
15	Pegmatite quartz	Kawamata, 〃	99.75	0.305	6230	—	—	380
16	Rock crystal	Brazil	99.95	0.250	Standard	153.59	0.79117	very large

when fired in air, in steam, or in reducing atmosphere of carbon monoxide.

2) Those specimens of quartz rock which contain more impurities and smaller activation energy of the sluggish inversion, have larger spacings and larger line breadth.

3) The lattice distortion caused by the formation of solid solution would be one of the causes which lower the activation energy of the sluggish inversion.

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Thermal Decomposition of Chromic Anhydride Supported on Alumina

By Yoshio MATSUNAGA

(Received June 9, 1958)

In our previous papers[1,2] we have described the anomalous oxidation of supported chromia associated with its highly dispersed structure and have presented a new method of examining the structure of chromia-alumina and chromia-zinc oxide catalysts. In the infinite two-dimensional dilution of chromium, it has been shown that chromia is oxidized completely to chromic anhydride. This chemical change is in sharp contrast to our knowledge of the thermal decomposition of chromic anhydride to chromia. The anomalous stability of the plus-six oxidation state of chromium in a highly dispersed state has been explained by the relative importance of surface oxidation of chromia. The present work has as its purpose the confirmation of this stabilization of the higher oxidation state by a study of the thermal decomposition of supported chromic anhydride.

Experimental

Gamma-alumina prepared by the method described in the previous paper[1] was chosen as a carrier because of its high surface area and of its lack of reactivity. Samples were prepared by impregnation with chromic acid solution. They were allowed to stand overnight, filtered, and dried at 110°C. Thermal decomposition was carried out in a stream of oxygen for five hours at 300, 350 and 450°C. A part of the sample, heated at 350°C, was reduced in a stream of hydrogen for five hours at 360°C for the purpose of applying the susceptibility-composition isotherm method[3] to the product. The magnetic susceptibility measurements and the determination of the mean oxidation number of chromium were described previously. The alumina used in this work was found to have a susceptibility of -0.36×10^{-6} per gram.

Results and Discussion

Fig. 1 shows the mean oxidation number of chromium, determined by an iodometric titration, plotted against the chromium content. Glemser et al.[4] showed that chromic anhydride begins to decompose in a stream of oxygen above 250°C, the products being $CrO_{2.6}$ in the temperature range from 283 to 314°C, $CrO_{2.4\sim5}$ from 334 to 388°C, and $CrO_{1.6}$ above 400°C. As the chromium content increases, it would be expected that the compositions of the products in the present system would become close to those reported by Glemser provided that samples are heated in the same temperature ranges. We chose 300, 350, and 450°C as the representative conditions of the above-mentioned three temperature ranges. The curves in Fig. 1 indicate clearly that the plus-six oxidation state is stabilized by the dispersed structure and even at 450°C chromic anhydride in the infinite two-dimensional dilution does not decompose at all. On the other hand, in the higher content range of chromium, the compounds $CrO_{2.6}$ and $CrO_{2.4\sim5}$ which appear in the thermal decomposition of massive chromic anhydride, are not found in our samples. These intermediate oxides seem to be insufficiently stable to exist in the dispersed state.

1) Y. Matsunaga, This Bulletin, **30**, 868 (1957).
2) Y. Matsunaga, ibid., **31**, 58 (1958).
3) R. P. Eischens and P. W. Selwood, *J. Am. Chem. Soc.*, **69**, 1590, 2693 (1947).
4) O. Glemser, U. Hauschild and F. Trüpel, *Z. anorg. u. allgem. Chem.*, **277**, 113 (1954).

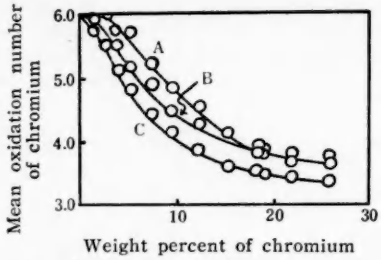

Fig. 1. Relation of oxidation number of chromium supported on gamma-alumina to its content.
A, chromic anhydride was decomposed at 300°C; B, at 350°C; C, at 450°C.

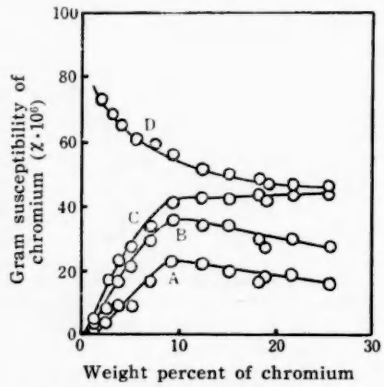

Fig. 2. Susceptibility-composition isotherm for chromium in its oxides supported on gamma-alumina.
A, chromic anhydride was decomposed at 300°C; B, at 350°C; C, at 450°C; D, reduced to chromia.

The gram susceptibility of the chromium ion, calculated on the assumption that the magnetic contributions of the chromium, aluminum, and oxygen ions are additive, is shown in Fig. 2. The chromium in the plus-six oxidation state has no unpaired electron and the estimated susceptibility based on the value for chromic anhydride[5] is 1×10^{-6}, so the decrease of the susceptibility value to almost zero, accompanying the dilution, means an increase of oxidation number to plus-six.

The relationships of the oxidation number and the magnetic susceptibility of chromium to its content in the samples treated at 450°C bear close resemblance to the similar ones shown in the previous paper. It is suggested that the same product is given by the heat-treatment at 450°C regardless of the starting materials; chromic anhydride or chromic oxide. The oxidation number in the series treated at 300 and 350°C are appreciably higher than four in the content range of chromium, less than that corresponding to point *l* in the susceptibility-composition isotherm of the reduced samples. Although we can not find any marked difference between the oxidation numbers of chromium in the samples decomposed at 300 and at 350°C, which contain more than 15% of chromium, the susceptibility values in the series treated at 350°C are significantly larger than thsoe in the series treated at 300°C. Such an increase of susceptibility value without the change of oxidation number suggests the occurrence of a structural change in chromium oxide. The samples containing less than 15% of chromium continue to lose a considerable amount of oxygen between 300 and 350°C.

As shown in Fig. 3, the thermal decomposition of chromic anhydride in the dispersed state occurs continuously, and it seems that the oxidation state of chromium changes from plus-six to plus-three without taking intermediate oxidation states. This view is consistent with the fact that there is only one kind of catalytically-active center for the decomposition of aqueous hydrogen peroxide on the surface of the oxidized chromia-alumina catalysts throughout the range of mean oxidation number of chromium from 3.12 to 5.65[6].

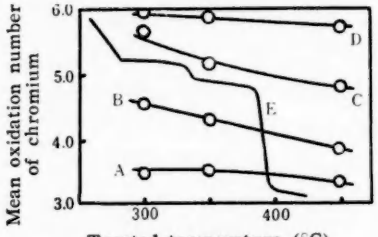

Fig. 3. Relation of oxidation number of chromium to treated temperature in the thermal decomposition of chromic anhydride.
Chromium content A, 27 percent; B, 12.5 percent; C, 5.5 percent; D, 1.8 percent; E, massive chromic anhydride (after Glemser et al.).

Consequently, it appears that the relatively large and thick aggregates of chromic anhydride on the surface of alumina

5) F. W. Gray and J. Dakers, *Phil. Mag.*, **11**, 297 (1931).

6) Y. Matsunaga, This Bulletin, **30**, 984 (1957).

lose the greater part of their active oxygen below 300°C and only a small amount between 350 and 450°C. (cf. curve A in Fig. 3) This anomaly seems to be due to the instability of the intermediate compounds $CrO_{2.6}$ and $CrO_{2.4\sim5}$. There is no loss of oxygen between 300° and 350°C, but the product continues the structural change to chromia in this temperature range and completes it between 350° and 450°C. As described in the previous paper, the surface-accessible sites and some vacant sites due to lattice defects accommodate excess of oxide ions so the apparent oxidation number in the final product is always higher than plus-three. The smaller aggregates of chromium oxide are more defective and have higher surface area, so they have larger accommodation capacity for excess of oxygen. Therefore, the stabilization of the plus-six oxidation state becomes more effective as the chromium content decreases and the size of aggregates becomes smaller. The continuous loss of oxygen throughout the whole temperature range suggests that the product from small aggregates is highly defective and has no definite structure. (cf. curves C and D in Fig. 3)

In the previous paper we showed that the study of the oxidation of the chromia-alumina catalyst system by chemical analysis may be as useful as the susceptibility-composition isotherm method proposed by Selwood. However, the thermal decomposition of chromic anhydride on alumina is a step which takes place practically in the preparation of this catalyst and we can point out easily the position of point *l* in curves B and C in Fig. 1 and curves A, B and C in Fig. 2. Therefore, in the process of preparation, it is possible to get directly the same useful information about the degree of dispersion of chromium as from the oxidation of the final products either by the chemical method or by the magnetic method.

Summary

The thermal decomposition of chromic anhydride supported on gamma-alumina at 300°, 350° and 450°C was examined by chemical analysis and by magnetic susceptibility measurements. The stabilization of the plus-six oxidation state of chromium in a highly dispersed state was confirmed by the present experiments. In addition, by comparing the oxidation number and the magnetic susceptibility of chromium, it was found that the behavior of supported chromic anhydride in large aggregates is also anomalous. Contrary to the case of the thermal decomposition of massive chromic anhydride, the intermediate oxides $CrO_{2.6}$ and $CrO_{2.4\sim5}$ were not found. The large aggregates of chromic anhydride on alumina lose the greater part of their active oxygen at relatively low temperatures and crystallize continuously into chromia with further loss of oxygen.

The author wishes to express his hearty thanks to Professor Akamatu for his kind direction.

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The Separation of Tellurite, Selenite and Sulfite Ions by Anion-Exchange Resins

By Akira IGUCHI

(Received February 14, 1958)

The separation of tellurite, selenite and sulfite is a difficult problem. A few ion-exchange separations of chloro complexes of tellurium and selenium have recently been reported[1,2]. In this paper the behavior of sulfite, selenite and tellurite towards anion exchange resins is studied in alkaline media. The results give a new successful separation of these oxy-acid anions.

Experimental

Materials. — *Anion-exchange resin.* — Air-dried Dowex 1-X8, 100- to 200-mesh, was used in either the hydroxide or the nitrate form.

Sodium tellurite and sodium selenite.—Guaranteed reagents were used without purification. The ordinary gravimetric analysis of these salts[3] showed that they were pure enough for the purpose of this study. The samples dissolved in water could not be kept for a long time, since the state of these salts in the aqueous solution changes with the lapse of time in a neutral solution; in an alkaline stock solution oxidation may occur, when they are kept too long. Hence the sample solution has been kept for 3 days at the longest, in a glass stoppered Erlenmeyer flask kept in a refrigerator.

Sodium sulfite.—The neutral aqueous solution of this salt decomposes only about 0.5% a day right after dissolution. But the rate of decomposition increases when the solution is kept longer. Thus it is desirable to dissolve the salt right before each experiment. On the anion-exchange resin of the hydroxide form, the sulfite ion seems to be more stable than in a neutral solution; the quantity of sulfite ions eluted from the resin is equal to that expected even after two days' keeping on the resin. The quantity of sulfite is estimated by the iodimetric titration.

Procedures. *Analysis of samples.*—The quantity of tellurite in the solution was determined by the titration of thiosulfate proposed by R. A. Johnson and D. R. Fredrickson[4]. The tellurite in the sample was potentiometrically titrated with standard iodine solution after the addition of hydrochloric acid, potassium iodide and a known quantity of thiosulfate. Ammonium salt did not cause interference even when its concentration was as high as 1.5 mol./l. Since a positive error is expected in a more concentrated solution, the effluent was diluted with a suitable amount of water to keep the concentration of ammonium salts less than 1.3 mol./l.

The quantity of selenite in the solution was determined by the titration method which was proposed by J. F. Norris and H. Fay[5], by the use of standard iodine solution, starch and a definite amount of thiosulfate. Of course the end point was also determined potentiometrically as in the case of tellurite.

The quantity of sulfite in the solution was titrated with standard iodine solution, together with acetic acid and glycerin[6].

The measurement of distribution coefficients of tellurite, selenite and sulfite ions in various concentrations of sodium nitrate and sodium hydroxide.—The distribution coefficient, K_d was measured by the column method. The K_d values of the ion were calculated from the volume of the eluant through the following equation,

$$K_d = (V - i)/M \quad [7\text{–}9] \qquad (1)$$

where K_d(cc./g.) is the distribution coefficient, V(cc.) the volume of eluant passed through the column until the concentration of the sample in the effluent becomes maximum, i(cc.) the interstitial volume of the column and M(g.) the weight of the resin. The columns were 7.0 mm. in diameter, and contained 1∼3 g. of the resin. The flow rate was less than 0.3 cc./min.

Results and Discussion

Relationship between the distribution coefficient of tellurite, selenite and sulfite and the concentration of nitrate or hydroxide ion in the eluant.—The results obtained with the procedure using aqueous solutions of sodium nitrate as eluants are shown in Fig. 1, and those with sodium hydroxide solutions in Fig. 2. The values are the mean values of the two

1) F. Aoki, This Bulletin, **26**, 480 (1953).
2) Y. Sasaki, ibid., **28**, 89 (1955).
3) e.g., F. P. Treadwell and W. T. Hall, "Analytical Chemistry" 8th English Ed., John Wiley & Sons, New York, (1935), Vol II, p. 268.
4) R. A. Johnson and D. R. Fredrickson, *Anal. Chem.*, **24**, 866 (1952).
5) J. F. Norris and H. Fay, *J. Am. Chem. Soc.*, **23**, 119 (1900).
6) A. Kurtenacker and R. Wollak, *Z. anorg. u. allgem. Chem.*, **161**, 201 (1927).
7) M. Honda, "Ion Exchange" (Ion Kokan) (in Japanese), Nankodo, Tokyo, Japan. (1954) p. 95.
8) D. DeVault, *J. Am. Chem. Soc.*, **65**, 532 (1943).
9) J. N. Wilson, ibid., **62**, 1583 (1940).

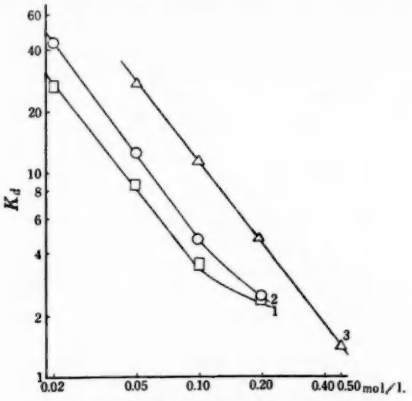


Fig. 1. Relationship between K_d and the concentration of sodium nitrate in the eluant.
1: Sodium tellurite. 2: Sodium selenite.
3: Sodium sulfite.

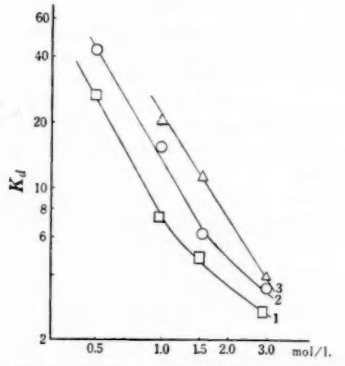


Fig. 2. Relationship between K_d and the concentration of sodium hydroxide in the eluant.
1: Sodium tellurite. 2: Sodium selenite.
3: Sodium sulfite.

experimental data and the error is less than about 2%.

When the reaction of the ion with the ion-exchanger is supposed to be

$$\nu RX + A^{\nu-} = R_\nu A + \nu X^-$$

the distribution coefficient K_d is given by the equation,

$$K_d = [R_\nu A]/[A^{\nu-}] \qquad (2)$$

and the equilibrium constant K_{ex} is given by the equation,

$$K_{ex} = [R_\nu A][X^-]^\nu / [RX]^\nu [A^{\nu-}] \qquad (3)$$

From equations 2 and 3 it is seen that

$$K_d = K_{ex} \cdot [RX]^\nu / [X^-]^\nu \fallingdotseq k/[X^-]^\nu \qquad (4)$$

where k is a constant.

So the equations 5 and 6 are obtaind:

$$\log K_d = \log k - \nu \log [X^-] \qquad (5)$$

or
$$d \log K_d / d \log [X^-] = -\nu \qquad (6)$$

Consequently from the slope of the curve, it is possible to induce the charge of the exchanged ion.

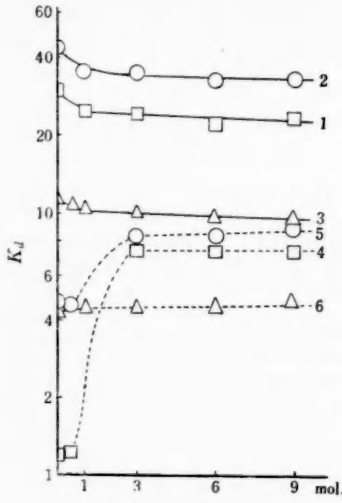
From Figs. 1 and 2, linear relationships of log K_d towards log C are observed except in the region of high concentrations of the eluants. The linear lines for tellurite, selenite and sulfite in Fig. 1 are almost parallel and their slope is about 1.5 at a low concentration. So they may contain the ions of one negative charge; in other words, $HTeO_3^-$, $HSeO_3^-$ may be present together with anions of two negative charges in these neutral solution.

The straight linesf or these salts in Fig. 2 are also almost parallel and their slope is about 2.0 at a low concentration, so they must exist in the form of anions with two negative charges, that is, TeO_3^{2-}, SeO_3^{2-} and SO_3^{2-} in these strongly alkaline solutions.

As the difference of K_d among these three anions is not very remarkable, and as the tailing part of selenite and tellurite in elution process is not sharp, it is very difficult to separate them by using sodium nitrate or sodium hydroxide solution as an eluant.

The relationship between the concentration of ammonia added and the distribution coefficient.—In the elution process of the column method, these anions are eluted too readily by neutral nitrate solution to be separated from each other, and with too great difficulty by hydroxide solution. Consequently it is necessary to study the intermediate region of pH of the eluant. But aqueous ammonia without salt cannot be used as the eluant, for these anions are not eluted with it in any concentration. Thus the effect of the addition of aqueous ammoia to the eluant containing nitrate or hydroxide was studied. The results are shown in Fig. 3.

By adding ammonia to a nitrate eluant, the values of the distribution coefficients, K_d, for tellurite and selenite increase rapidly, but the difference among the ions becomes smaller; therefore this combination is not suitable for the purpose of



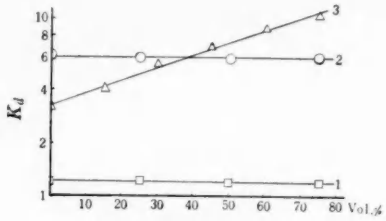
Ammonia in eluant

Fig. 3. Relationship between K_d and the concentration of added ammonia in eluant.
1: Sodium tellurite eluted with 0.4 N sodium hydroxide. 2: Sodium selenite eluted with 0.4 N sodium hydroxide. 3: Sodium sulfite eluted with 1.5 N Sodium hydroxide. 4: Sodium tellurite eluted with 0.1 mol./l. sodium nitrate. 5: Sodium selenite eluted with 0.1 mol./l. sodiumnitrate. 6: Sodium sulfite eluted with 0.2 mol./l. sodium nitrate.

separation. On the contrary, although the addition of ammonia to a hydroxide eluant causes only a small decrease of K_d, the difference of K_d for each anion remains unchanged and fortunately the tailing part of selenite and tellurite in the elution process is much shortened. Therefore the eluant containing 0.5 mol./l. of sodium hydroxide and 3.0 mol./l. of ammonia may be the most suitable for the separation of selenite and tellurite.

The effect of an organic solvent on the distribution coefficient.—In order to study the effect of an organic solvent on the distribution coefficient of these anions, the relationship between K_d and the percentage of added ethanol was examined. The concentration of nitrate and ammonia are kept constant, i.e. 0.1 mol./l. of sodium nitrate and 0.5 mol./l. of ammonia for tellurite and selenite, and 0.2 mol./l. of sodium nitrate and 0.5 mol./l. of ammonia for sulfite. Results are shown in Fig. 4A.

From the results thus obtained considerable differences are recognized among selenite, tellurite and sulfite. The distribution coefficient of sulfite increased with the increase of the concentration of ethanol, while the coefficients of the other two ions remain almost constant even up to 75% of ethanol.

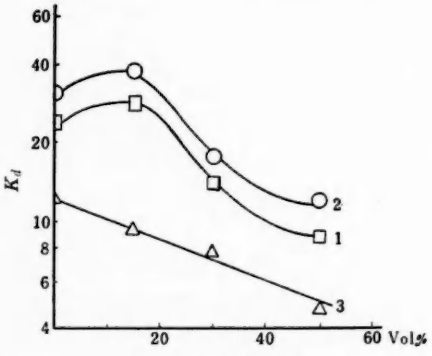


Ethanol in eluant

Fig. 4A. Relationship between K_d and the percentage of added ethanol. The eluants contained also 0.5 mol./l. of ammonia.
1: Sodium tellurite eluted wilh 0.1 mol./l. sodium nitrate. 2: Sodium selenite eluted with 0.1 mol./l. sodium nitrate. 3: Sodium sulfite eluted with 0.2 mol./l. sodium nitrate.

These results seemed to suggest a promising method of separating sulfite from selenite or tellurite, but the tailing part of tellurite or selenite is not sharp in the elution process, and no satisfactory result was obtained even with fairly long columns containing up to 5.0 g. of resins. This separation may be completed, when a much longer column is used.

In case of sodium hydroxide eluants,



Ethanol in eluant

Fig. 4B. Relationship between K_d and the percentage of added ethanol. The eluant contained also 3.0 mol./l. of ammonia.
1: Sodium tellurite eluted with 0.5 N sodium hydroxide. 2: Sodium selenite eluted with 0.5 N sodium hydroxide. 3: Sodium sulfite eluted with 1.5 N sodium hydroxide.

the relationships between K_d and the percentage of ethanol are shown in Fig. 4B. The concentration of sodium hydroxide is 0.5 mol./l. for the tellurite and selenite, and 1.5 mol./l. for sulfite; the concentration of ammonia is 3.0 mol./l. in both cases.

As shown in Fig. 4B, the distribution coefficient of sulfite decreases as the concentration of ethanol increases, and this is a result in contrast to that of nitrate eluant. This fact may be due to the decrease of the dissociation of HSO_3^- ion.

But in cases of tellurite and selenite, the K_d increased up to 20% of ethanol and beyond this value began to decrease. When 50% of ethanol was added to the eluant, tellurite and selenite were eluted more easily, though the separation of selenite and tellurite is not so clear-cut. Therefore, this method can be used only for separating selenite, or tellurite from sulfite by using 5.0 g of Dowex 1-X8 resin column (in Figs. 5A and 5B).

The separation of tellurite, selenite and sulfite.—From the result of Fig. 3, the eluant containing 0.5 mol./l. of sodium hydroxide and 3.0 mol./l. of ammonia is expected to be suitable for separating tellurite from selenite. Then sulfite can be eluted by 2.0 mol./l. of sodium hydroxide solution.

The column of the size 1.0×13.0 cm. containing 5.0 g. of Dowex 1-X8 (analytical grade) was used. One of the typical examples of the perfect separation is shown in Fig. 6. The collected tellurite, selenite and sulfite are titrated by the methods described before.

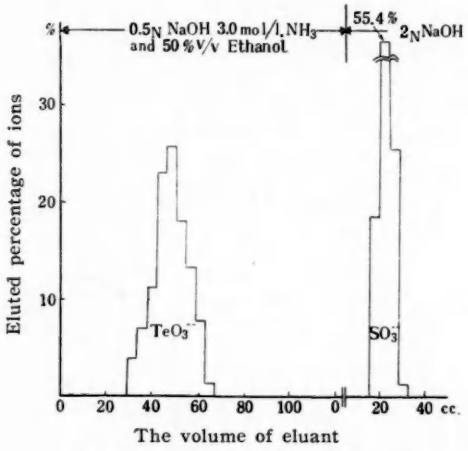


Fig. 5A. Elution curve of mixed sample of tellurite and sulfite. (The flow rate is 0.1 cc./min.)

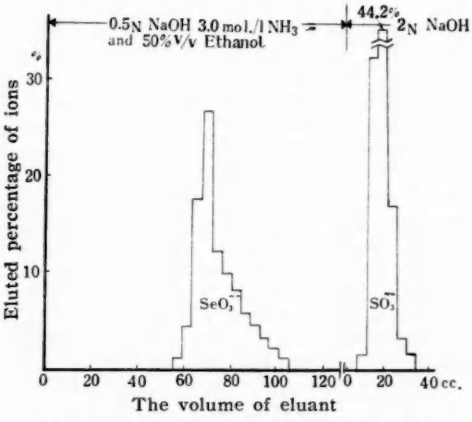


Fig. 5B. Elution curve of mixed sample of selenite and sulfite. (The flow rate is 0.1 cc./min.).

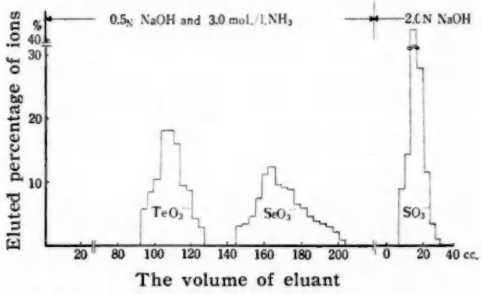


Fig. 6. Elution curve of mixed sample. (The flow rate is 0.1 cc./min.)

The analysis of the mixture of tellurite, selenite and sulfite.—This method of separation was applied to a mixture of known quantities of these salts and the results obtained are shown in Table I. Each value is the mean value of the four repeated experiments.

When the sample solution of tellurite was not fresh or the elution process was too prolonged, the recovery of tellurite was decreased. Therefore, it is desirable to use a newly prepared sample and to shorten the time of analysis. When resins of larger grain size are used, the clear-cut separation is not obtained. Difficulties in handling these intractable materials, for example, the changes of the state in the solution, cause a small discrepancy between the data of recovery and the theoretical values.

TABLE I
THE ANALYSIS OF MIXED SAMPLES

		Sample I		Sample II	
		mmol.	%	mmol.	%
Tellurite	Added values	0.0712_5	100	0.142_5	100
	Observed values	0.0705_5	99.2±0.21	0.141_1	99.0±0.23
Selenite	Added values	0.134_6	100	0.188_5	100
	Observed values	0.123_8	98.0±1.8	0.183_4	97.5±2.5
Sulfite	Added values	0.100_9	100	0.117_8	100
	Observed values	0.0996_9	98.8±1.6	0.116_3	98.7±1.3

Summary

1. The distribution coefficients of tellurite, selenite and sulfite in neutral nitrate solution and alkaline hydroxide solution were measured and the results suggest the presence of an acid salt ion HXO_3^- in neutral solution.

2. By the addition of ammonia to the eluant solution, the distribution coefficient of these salts in nitrate solution was increased, but in hydroxide solution it was decreased.

3. By the addition of ethanol to the eluant solution containing nitrate and ammonia, the distribution coefficient of sulfite increased, but that of tellurite and selenite remained constant even up to 75%. On the contrary, in the addition of ethanol to the hydroxide solution, the distribution coefficient of sulfite decreased, while that of tellurite and selenite increased at first and then decreased.

4. By using these results a complete separation of tellurite, selenite and sulfite was accomplished by the anion exchange chromatographic method using an alkaline eluant.

The author expresses his gratitude to Professor T. Shirai, Dr. Y. Yoshino and his colleagues in the laboratory both for their suggestions and for the discussion helpful in publishing this paper.

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π-Electronic Structures of α-Naphthoquinone and Anthraquinone

By Akira KUBOYAMA*

(Received March 13, 1958)

The *p*-quinone type compounds such as *p*-benzoquinone, α-naphthoquinone, and anthraquinone play an important role as oxidizing reagents in organic chemistry and biochemistry. As for their π-electronic structures, *p*-benzoquinone has already been studied by many workers but the theoretical work on α-naphthoquinone and anthraquinone is scanty[1]. Therefore, the π-electronic structure of α-naphthoquinone and anthraquinone is studied by the simple MO method.

Method of Calculations.—Because of the great discrepancy from the uniform distribution of π-electron density in quinones, which is due to the existence of electronegative oxygen atoms, it is desirable to use the self-consistent method which was used in our previous paper[2] concerning *o*- and *p*-benzoquinones. But the application of this method to α-napthoquinone and anthraquinone is difficult, since these molecules contain too many π-electrons compared with *p*-benzoquinone.

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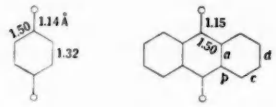
1) a) D. Hadzi, *Arkiv. Kem.*, **25**, 33 (1953); b) M. L. Josien and J. Deschamps, *J. chim. phys.*, **52**, 213 (1955); c) J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 4567 (1956).

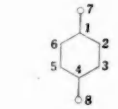
2) S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 499 (1953); S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, **76**, 1003 (1954).

Now, as is seen in the following X-ray diffraction data[3], the bond lengths of the C=O bond and the adjacent C—C bond are

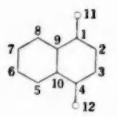


a,b,c,d = 1.38–1.40Å

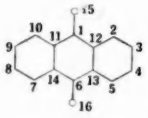
nearly equal in *p*-benzoquinone and anthraquinone, and the structures of the two six-membered carbon rings of anthraquinone are similar to that of the benzene nucleus. In view of these facts, we assumed the coulomb (α_i) and exchange (β_{ij}) integrals for α-naphthoquinone and anthraquinone as follows:



$$\alpha_{C_2}=\alpha_{C_3}=\alpha \quad \alpha_O=\alpha+1.3\beta$$
$$\alpha_{C_1}=\alpha+0.2\beta$$
$$\beta_{1-7}=\beta \qquad \beta_{1-2}=0.8\beta$$
$$\beta_{2-3}=1.1\beta$$



$$\alpha_{C_2}=\alpha_{C_{10}}=\alpha_{C_5}=\alpha_{C_6}=\alpha$$
$$\alpha_O=\alpha+1.3\beta \quad \alpha_{C_1}=\alpha+0.2\beta$$
$$\beta_{1-11}=\beta_{9-10}=\beta_{10-5}=\beta_{5-6}=\beta_{6-7}=\beta$$
$$\beta_{1-2}=\beta_{1-9}=0.8\beta \quad \beta_{2-3}=1.1\beta$$

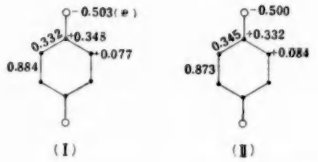


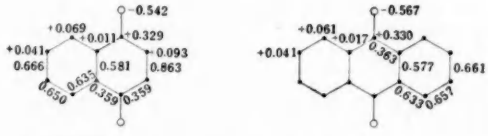
$$\alpha_{C_{12}}=\alpha_{C_2}=\alpha_{C_3}=\alpha$$
$$\alpha_O=\alpha+1.3\beta \quad \alpha_{C_1}=\alpha+0.2\beta$$
$$\beta_{1-15}=\beta_{12-13}=\beta_{12-2}=\beta_{2-3}=\beta_{3-4}=\beta \quad \beta_{1-12}=0.8\beta$$

Among these values, those concerning the quinone nuclei were made equal to the values evaluated for *p*-benzoquinone by the SCF method in the previous paper[2].

Results

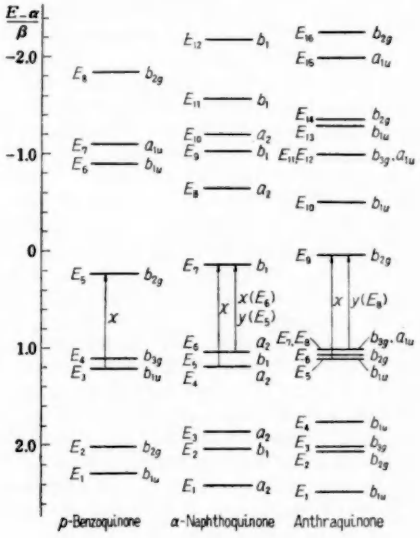
The obtained molecular diagrams and the energy levels are given below.





3) For *p*-benzoquinone; J. M. Robertson, *Proc. Roy. Soc.*, **150**, 106 (1935). For anthraquinone; S. N. Sen, *Indian J. Phys.*, **22**, 347 (1948).

The energy levels are classified according to the symmetry properties of the corresponding orbitals in the symmetry group of the molecule (D_{2h} for *p*-benzoquinone and anthraquinone, C_{2v} for α-naphthoquinone), taking the O—O direction as the *x*-axis and the molecular plane as the *xy* plane. The energy difference between the orbitals E_5 and E_6 of α-naphthoquinone is 0.003β. The letters *x* and *y* attached to the arrow showing the transition between the energy levels denote the directions of the polarization in the allowed transitions. The molecular diagram I for *p*-benzoquinone is the one previously calculated by the SCF method[2] and the diagram II for the same molecule is the one calculated by the present method. The agreement between these two molecular diagrams is satisfactory. Further, the energy levels of *p*-benzoquinone calculated by the two methods mentioned above are also in good agreement with each other. Thus, the results evaluated for α-naphthoquinone and anthraquinone may be thought to be nearly self-consistent.



Discussion

Molecular Diagrams. — The molecular diagrams of the three *p*-quinones are similar in many points. As for charge distributions, the negative charges of oxygen atoms slightly increase in the order *p*-benzoquinone, α-naphthoquinone and anthraquinone. The dipole moment (ca. 2.2 D) of α-naphthoqueinone calculated under

the assumption that the angle between the two carbonyl bond axes is 180°, is considerably larger than the measured value[4] (1.30 D) in which the contribution (ca. 0.6 D) of the atomic polarisation[5] characteristic of *p*-quinones is contained. Therefore the calculated dipole moment seems too large, though its value is thought to be considerably affected by the angle between the two carbonyl bond axes.

As for bond orders, the value for the C_2—C_3 bond is nearly equal in α-naphthoquinone and *p*-benzoquinone. Furthermore, the above diagrams show that the six-membered carbon rings of α-naphthoquinone and anthraquinone are properly approximated by the benzene nucleus. The bond orders of the two bonds, C_1—C_2, C_1—C_9 of α-naphthoquinone are equal. B. Pullman and J. Deudel[6] also obtained a similar result in their work on 1,2-benzanthra-3,4-quinone. From these results, it seems probable that the bond orders of the C—C bonds adjacent to the C—O bonds in quinones can hardly be affected by side carbon atom groups.

Energy Levels.—From the energy levels given above, the following two points are worthy of notice. First, the difference between the highest filled and the lowest vacant orbitals is similar in these *p*-quinones. This result explains a similarity among the π—π transition bands of the three *p*-quinones in the long-wavelength region, that is to say, they have a relatively weak band*1 near 300 mμ and a strong band near 250 mμ, respectively. The bands near 250 mμ are assigned as $E_3 \rightarrow E_5$ (*p*-benzoquinone), $E_4 \rightarrow E_7$ (α-naphthoquinone), and $E_5 \rightarrow E_9$ (anthraquinone), and the bands near 300 mμ as $E_4 \rightarrow E_5$ (*p*-benzoquinone), $E_5, E_6 \rightarrow E_7$ (α-naphthoquinone) and $E_6, E_7, E_8 \rightarrow E_9$ (anthraquinone). The fact that the intensity of the band near 300 mμ of *p*-benzoquinone is about ten times weaker than that of α-naphthoquinone and of anthraquinone can be explained with the present result that in *p*-benzoquinone alone, the corresponding transition is forbidden.

Second, the energy levels as a whole are a little elevated as the size of the *p*-quinone molecule becomes larger. This result can be anticipated considering the ratios of the number of electronegative oxygen atoms to that of far less electronegative carbon atoms in each *p*-quinone molecule. As a measure of the elevation of the energy levels, the average value of the highest filled and the lowest vacant orbital energies of each *p*-quinone may be adopted. This value has $\alpha+0.665\beta$, $\alpha+0.577\beta$, and $\alpha+0.514\beta$ for *p*-benzoquinone, α-naphthoquinone, and anthraquinone, respectively. Now, the lone-pair orbital energies of the oxygen atoms in the three *p*-quinones are thought to be nearly equal. Then, it may be expected that the n-π transition energy becomes greater in the order of *p*-benzoquinone, α-naphthoquinone and anthraquinone. The observed phenomenon[1c,2] agrees satisfactorily with this expectation. It seems sure that the same explanation can be applied to the same phenomenon observed in *o*-quinones[1c,2].

The Effect of the Electron-Donating Substituent on the π—π Transition Bands.—In our previous work[7], the effect of the alkyl groups on the near UV absorption bands of *o*- and *p*-benzoquinones are studied using a modified form of Herzfeld-Nagakura-Baba's formula[8]. In a one-electron transition (m orbital $\rightarrow n$ orbital), the shift in wave numbers ($\Delta\nu_{m\rightarrow n,i}$) due to a substitution on the ith carbon atom in a quinone molecule has the value,

$$\Delta\nu_{m\rightarrow n,i} = K_m C_{mi}^2 - K_n C_{ni}^2 \qquad (1)$$

Here, the two conditions are required, that m and n orbitals are non-degenerate and the m orbital energy is higher than the substituent's lone-pair orbital energy. C_{mi} and C_{ni} are the coefficients of the ith atomic orbital in the LCAO MO, m and n, respectively. K_m and K_n are nearly constant if the kind of substituent is fixed, and $K_m < K_n < 0$. So, if $C_{mi}^2 \geq C_{ni}^2$, $\Delta\nu_{m\rightarrow n,i} < 0$. Then, the greater the C_{mi}^2 value is and the smaller the C_{ni}^2 value, the greater the extent of the red-shift of the band is. Thus, considering the C_{mi}^2 and C_{ni}^2 values, the magnitude of the red shift of a band by a substituent can be presumed.

Now, let us apply the above method to α-naphthoquinone and anthraquinone whose data are given in Figs. 1[9] , 2[10] and

4) B. Eda, Presented at the Symposium on Structural Chemistry, Sendai (1954).
5) R. J. W. LeFèvre, "Dipole Moments", Methuen & Co. Ltd., London (1948), p. 100.
6) B. Pullman and J. Daudel, *Compt. rend.*, **238**, 964 (1954).
*1 In view of the intensity and the solvent effect, this band is thought to be due to π-π transition.
7) A. Kuboyama *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1062 (1956).
8) K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947); H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 72 (1951).
9) M. O'L Crowe, *J. Biol. Chem.*, **115**, 479 (1936).
10) R. A. Morton and W. T. Earlam, *J. Chem. Soc.*, **1941**, 159.

Tables I, II. In Figs. 1 and 2, in all cases, the substituent is the hydroxyl group and the solvent ethanol. Since the solvent effect[9] of ethanol on the bands near 250 mμ and 300 mμ of α-naphthoquinone are very small compared with the substitution effect, the former effect may safely be

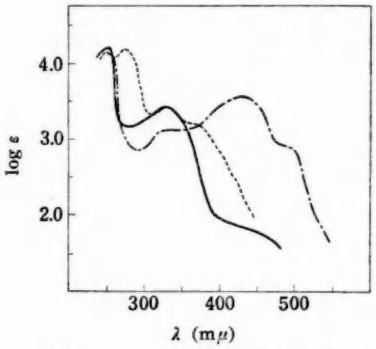


Fig. 1. ——, 1, 4 Naphthoquinone;
- - - -, 2-Hydroxy- 〃 ;
— - —, 5-Hydroxy- 〃 ;
Solvent, Ethanol.

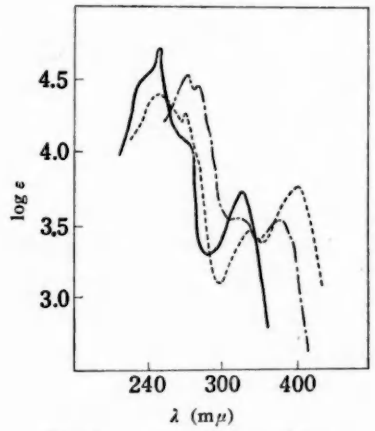


Fig. 2. ——, Anthraquinone;
- - - -, 2-Hydroxy- 〃 ;
— - —, 3-Hydroxy- 〃 ;
Solvent, Ethanol.

TABLE I

THE SQUARE VALUES OF THE COEFFICIENTS IN α-NAPHTHOQUINONE (THE NUMBERS IN THE FIRST ROW DENOTE THE POSITIONS OF THE SUBSTITUTIONS)

	2	5	6
$E_4(a_2)$	0.270	0.001	0.017
$E_5(b_1)$	0.000	0.298	0.073
$E_6(a_2)$	0.085	0.000	0.207
$E_7(b_1)$	0.082	0.036	0.028

TABLE II

THE SQUARE VALUES OF THE COEFFICIENTS IN ANTHRAQUINONE

	2	3
$E_5(b_{1u})$	0.001	0.098
$E_6(b_{2g})$	0.136	0.032
$E_7(b_{3g})$	0.000	0.125
$E_8(a_{1u})$	0.167	0.042
$E_9(b_{2g})$	0.032	0.031

neglected. All the π-orbitals of α-naphthoquinone and anthraquinone are intrinsically non-degenerate and we can reasonably assume that the lone-pair orbital energy of the oxygen atom in the hydroxyl group as a substituent is lower than the E_4(α-naphthoquinone) and E_5(anthraquinone) orbital energies. Thus, the above method can be applied. As the consequence it may be expected that, as for α-naphthoquinone, the band near 250 mμ largely shifts towards longer wave lengths for 2-substitution and remains almost constant for 5-substitution. The data in Table I clearly fit these expectations. On the other hand, the bands near 300 mμ split into the two bands for both 2- and 5-substitutions, and from the data in Table I, the longer-wavelength bands are thought to correspond to the transitions, $E_6 \rightarrow E_7$ (2-substitution) and $E_5 \rightarrow E_7$ (5-substitution), and the shorter wavelength bands to the transitions, $E_5 \rightarrow E_7$ (2-substitution) and $E_6 \rightarrow E_7$ (5-substitution). As for anthraquinone, the band near 250 mμ largely shifts towards longer wavelengths for 3-substitution and scarcely shifts at all for 2-substitution. This fact is clearly explained from eq. (1), and C_{mi}^2 and C_{ni}^2 values given in Table II. It is thought that the band near 300 mμ of unsubstituted anthraquinone is mainly contributed by the transition, $E_8 \rightarrow E_9$, since this transition alone is allowed among the three transitions assigned to this band, but in hydroxy anthraquinone the forbidden transitions come to be allowed to some extent by the perturbation of the substituent group. From the coefficient values in Table 2, it may be induced that the longest wavelength max. of the band near 300 mμ corresponds to the transition $E_8 \rightarrow E_9$ for 2-substitution and $E_7 \rightarrow E_9$ for 3-substitution, respectively. These assignments seem reasonable from the fact that the intensity of the absorption band under consideration is stronger in 2-hydroxy anthraquinone than in 3-hydroxyl derivative (see Fig. 2). Thus, the above theoretical consideration can clearly explain the effect

of the electrondonating substituent on the $\pi-\pi$ transition bands in the near UV region of α-naphthoquinone and anthraquinone.

In addition, as for the report[11] that in the α-naphthosemiquinone ion the probability of finding the unpaired electron in a $p_z\pi$ orbital centered on the 2nd carbon atom is ca. ten times greater than that in a $p_z\pi$ orbital centered on the 5th or 6th carbon atoms, the probabilities are thought to be approximately parallel to the C_{7i}^2 values and the result in Table I is unsatisfactory in comparison with the experimental result, but a similar trend is seen for the *o*-benzosemiquinone ion[11b,*2],

Summary

Electronic structures of *p*-benzoquinone, α-naphthoquinone, and anthraquinone were studied with the simple MO method, using the same integral values as adopted in the SCF MO calculation for *p*-benzoquinone. As for charge distributions, the negative charges of oxygen atoms slightly increase in the order *p*-benzoquinone, α-naphthoquinone and anthraquinone. The calculated dipole moment (2.2 D) of α-naphthoquinone seems too large. As for bond orders, the reasonable results were obtained. Two problems concerning the near UV absorption bands (1. a similarity among the $\pi-\pi$ transition bands of the three *p*-quinones, 2. a relative magnitude of the $n-\pi$ transition energy in the order of *p*-benzoquinone, α-naphthoquinone and anthraquinone) can be clearly explained with the calculated results. Especially, the effect of the electrondonating group on the $\pi-\pi$ transition bands of α-naphthoquinone and anthraquinone can also be favourably explained, according to the modified Herzfeld-Nagakura-Baba's formula, with the calculated results. It seems sure that for the *o*-quinone type compounds the similar result can be obtained with the same method as used for the *p*-quinone type compounds.

The author wishes to express his sincere thanks to Professor S. Nagakura of the Institute for Solid State Physics, Tokyo University, for his kind guidance.

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11) a) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **24** 479 (1956); b) H. M. McConnell, ibid., **24**, 632 (1956).
*2 In our previous calculation[2], the similar result to 11b) was obtained.

The Action of Hydrogen Bromide and Oxygen on Various Ethenoid Compounds. III. The Steric Effects of the Bromo Free Radicals Produced from Various Ethenoid Compounds on the Reactivities with Oxygen

By Makoto TAKAHASI

(Received March 18, 1958)

The mechanism of the action of hydrogen bromide on various ethenoid compounds in the presence of a large amount of oxygen has been discussed in the preceding papers of this series[1,2], and the fundamental reaction scheme has been assumed as follows:

(1) $\rangle C=C\langle + O_2 + HBr \longrightarrow$
$Br\cdot$ (initiation)

(2) $\rangle C=C\langle + Br\cdot \longrightarrow$
$\succ C-C\lessdot$ (propagation)
Br

(3) $\succ C-C\lessdot + O_2 \longrightarrow$
Br
$\rangle C-C\lessdot$ (propagation)
$\cdot O_2 \quad Br$

1) M. Takahasi, This Bulletin, **29**, 625 (1956)
2) M. Takahasi, ibid., **29**, 973 (1956).

(4) $\rangle C(\cdot O_2)-C\langle + HBr \longrightarrow$

$\rangle C(HO_2)-C\langle + Br\cdot$ (propagation)

(5) $\rangle C(HO_2)-C\langle + HBr \longrightarrow$

oxidation products $+ Br\cdot$ (propagation)

(6) $\rangle C(\cdot)-C\langle + Br_2 \longrightarrow$

$\rangle C(Br)-C\langle + Br\cdot$ (propagation)

(7) $Br\cdot + Br\cdot \longrightarrow Br_2$ (termination)

(8) $\rangle C(\cdot)-C\langle + Br\cdot \longrightarrow$

$\rangle C(Br)-C\langle$ (termination)

From the kinetical point of view, it is desirable to establish a complete method to determine the velocity constants of these reactions, but at present it may be difficult to carry out a kinetical study of the reactions of the three component systems The author attempted to study qualitatively the reactions of bromine with ethenoid compounds, such as β-methylcinnamic acid, cinnamic acid, *p*-methoxycinnamic acid, atropic acid, and diphenylethylene, to compare the intermediate bromo free radicals to be produced from these ethenoid compounds in the reactivity with oxygen, expecting that it may be helpful to elucidating the mechanism of the reactions of hydrogen bromide and oxygen with ethenoid compounds, because the reactions are presumed to include the same reaction processes as 2,3,6,7, and 8 as shown below:

(1′) $Br_2 \longrightarrow 2\,Br\cdot$ (compare with process 1)

(2′) $Br\cdot + \rangle C{=}C\langle \longrightarrow$

$\rangle C(\cdot)-C\langle$ (same as process 2)

(3′) $\rangle C(\cdot)-C\langle + O_2 \longrightarrow$

$\rangle C(\cdot O_2)-C\langle$ (same as process 3)

(4′) $\rangle C(\cdot O_2)-C\langle +$ hydrogen donor $\longrightarrow$

$\rangle C(HO_2)-C\langle$ (compare with process 4)

(5′) $\rangle C(HO_2)-C\langle \xrightarrow{\text{thermal or acid decomposition}}$

oxidation products (compare with process 5)

(6′) $\rangle C(\cdot)-C\langle + Br_2 \longrightarrow$

$\rangle C(Br)-C\langle$ (same as process 6)

(7′) $Br\cdot + Br\cdot \longrightarrow Br_2$ (same as process 7)

(8′) $\rangle C(\cdot)-C\langle + Br\cdot \longrightarrow$

$\rangle C(Br)-C\langle$ (same as process 8)

If any hydrogen donor such as hydrogen bromide does not exist, reaction 4′ does not proceed, and no bromohydroperoxide is produced. R. F. Brown and F. Daniels[3] observed the rate of the reaction of cinnamic acid with bromine in the absence of a hydrogen donor is reduced by the presence of oxygen in the light, and O. Simamura[4] observed the same effect of oxygen to occur even in the dark. J. L. Magee and F. Daniels[5] ascribed the inhibitive action of oxygen to the reaction of the bromo free radical with oxygen and to the reaction of the bromohydroperoxide radical thus produced with another bromo free radical, giving a peroxide or further oxidation products with evolution of a large amount of heat.

$C_6H_5-CH(O_2\cdot)-CH(Br)-COOH \longrightarrow$

$C_6H_5-CH(\cdot)-CH(Br)-COOH$

$C_6H_5-CH(O\cdot)-CH(Br)-COOH$

$C_6H_5-CH(O\cdot)-CH(Br)-COOH$

$\longrightarrow$ oxidation products such as benzoic acid.

The author attempted to identify the reaction products produced by the reactions of ethenoid compounds with bromine in the presence of an excess of oxygen. The ethenoid compounds, except β-methylcinnamic acid and diphenylethylene, did

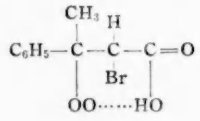
3) R. F. Brown and F. Daniels, *J. Am. Chem. Soc.*, **62**, 2820 (1940).
4) O. Simamura, This Bulletin, **17**, 274 (1942).
5) J. L. Magee and F. Daniels, *J. Am. Chem. Soc.*, **62**, 2825 (1940).

not give any appreciable amounts of oxidation products other than dibromides by the reactions with bromine in nonpolar solvents in spite of the presence of a large amount of oxygen, and the inhibitive action by oxygen was not remarkable. However, the reaction of β-methylcinnamic acid with bromine in the presence of a large amount of oxygen manifested a remarkable feature, as described below.

When oxygen was passed through a benzene solution of β-methylcinnamic acid in the sunlight with simultaneous addition of a benzene solution of bromine, the color of bromine faded far less rapidly than without introduction of oxygen. The reaction products were found to consist of carbon dioxide, acetophenone, a small amount of β-methylcinnamic acid dibromide, and some unidentified aldehyde.

Further, the reaction of β-methylcinnamic acid with hydrogen bromide and oxygen was carried out, and the reaction products were found to include carbon dioxide, α-bromoacetophenone and *p*-bromophenol, and a large amount of β-methylcinnamic acid was recovered, while β-methylcinnamic acid dibromide could not be detected in the products. It is to be noted that the reaction products in this case do not correspond to those of the reaction of cinnamic acid with hydrogen bromide and oxygen[1]. *p*-Bromophenol formed may inhibit the progress of the reaction of β-methylcinnamic acid with hydrogen bromide and oxygen.

Generally, in the reactions of ethenoid compounds with bromine in the presence of a large amount of oxygen, no hydrogen donor apparently exists. However, if acetophenone is formed in the reaction of β-methylcinnamic acid with oxygen and bromine via a bromohydroperoxide formation, reactions 4′, and 5′, it is necessary to assume the presence of a hydrogen donor. Although no evidence for either an intra- or an inter-molecular hydrogen transfer is available, it seems probable that the hydrogen of the carboxyl group moves to the peroxidic oxygen to give a bromohydroperoxide, considering the relative positions of the carboxyl group and the peroxidic oxygen. The structure of the intermediate was presumed to be



The special reactivity of β-methylcinnamic acid with oxygen, compared with other ethenoid compounds, may be understandable from following consideration.

The yields of oxidation products in the reactions of the ethenoid compounds with oxygen and bromine are not directly related with the structures of the ethenoid compounds themselves, but depend on the reactivity of the bromo free radicals with oxygen. However, the discussions on the ethenoid compounds as described below may be helpful to understanding the reactivity of the bromo free radicals.

H. Suzuki[6], in his study on the absorption spectra of a series of stilbene derivatives, i.e. stilbene, α-methylstilbene, and α, β-dimethylstilbene, found that the absorption maxima of these compounds are shifted progressively in the order towards shorter wave lengths with increasing angles of twist of the phenyl groups out of the plane of the ethylenic linkage caused mainly by the steric repulsion between the methyl group and the phenyl group attached to different carbon atoms of the ethylenic linkage. In parallel with the study of the steric effect on the ultraviolet absorption spectra, H. Suzuki, O. Simamura and T. Ichihashi[7,8] studied the action of the bromine atom and oxygen on stilbene derivatives, and they found that the action of the bromine atom and oxygen on α, β-dimethylstilbene caused an oxidative cleavage of the double bond.

β-Methylcinnamic acid may be in a state of less steric strain than α,β-dimethylstilbene, because in the former the methyl group interacts only with one phenyl group, and the methyl and the phenyl group are attached to the same carbon atom of the ethylenic linkage. In the latter, the both methyl groups interact with the phenyl groups attached to different carbon atoms respectively, so that it may be in a state of a larger steric strain than β-methylcinnamic acid. Notwithstanding, in the series of cinnamic acid, β-methylcinnamic acid, and β-ethylcinnamic acid, the maxima of the absorp tion spectra are also shifted progressively in the order towards shorter wave lengths with decrease in extinction coefficients, as in the series of stilbene derivatives. This fact may indicate existence of a

6) H. Suzuki, This Bulletin, **25**, 145 (1952).
7) H. Suzuki, O. Simamura and T. Ichihashi, ibid., **27**, 235 (1954).
8) O. Simamura and H. Suzuki, ibid., **27**, 231 (1954).

steric repulsion between the methyl group and the phenyl group in β-methylcinnamic acid.

The amount of the steric strain of π-electron system caused by the repulsion between the methyl group and the phenyl group may be of the same order in the intermediate bromo free radical from β-methylcinnamic acid as in β-methylcinnamic acid, because the methyl group and the phenyl group are attached to the same carbon atom. Thus the reactivity of the bromo free radical produced from β-methylcinnamic acid with oxygen may be larger than the reactivity of the bromo free radicals produced from cinnamic acid and any other ethenoid compounds with no steric strain.

β-Methylcinnamic acid, α,β-dimethylcinnamic acid and diphenylethylene and the intermediate free radicals therefrom as well may be subject to a large steric strain. In α-methylcinnamic acid, however, the interaction of the α-methyl group with the β-phenyl group will be released at the stage of the intermediate bromo free radical, so that the reactivity of the bromo free radical produced from α-methylcinnamic acid with oxygen may not be large.

An experiment on the reaction of α-methylcinnamic acid with hydrogen bromide and oxygen was attempted, but no reaction took place. On the other hand, the experiment on the reaction of α,β-dimethylcinnamic acid with hydrogen bromide and oxygen by Simamura, Nomura, and the present author[9], which has not yet been published, showed that it gives α-bromoacetophenone and acetophenone by the reaction with hydrogen bromide and oxygen.

Diphenylethylene gave a large amount of the dibromide and a very small amount of *p*-bromophenol by the reaction with bromine and oxygen. This result is apparently inconsistent with the result discussed above. It is to be noted, however, that diphenylethylene has no reactive hydrogen in the molecule, so that the peroxide radical produced from oxygen and bromo free radical (reaction 4′), cannot give a bromohydroperoxide. In the case of α,β-dimethylstilbene, it may be possible that the methyl groups serve as hydrogen donors for the bromo peroxide radical by either an inter- or an intramolecular mechanism. Although the electronic effect of the methyl groups attached to the carbon atoms of the ethylenic linkage on the reactivity with bromine and oxygen has not been discussed, the present author considers such an effect as mentioned above possible, but at present no experimental evidence for the effect is available.

M. S. Kharasch, A. Fono, and W. Nudenberg[10] reported that diphenylethylene gave phenol and acetophenone by the reaction with hydrogen peroxide in the presence of perchloric acid. The present author also observed a special reactivity of β-methylcinnamic acid with hydrogen peroxide in the presence of perchloric acid. β-Methylcinnamic acid was decomposed to give carbonyl compounds, while cinnamic acid did not give any product under the same conditions. Investigation on the reaction is continued.

Experimental

Materials.—β-Methylcinnamic acid was synthesized by the Reformatsky reaction of acetophenone with ethyl iodoacetate in benzene, and recrystallized from ethyl alcohol, m.p. 104.5°. α-Methylcinnamic acid was synthesized by the Perkin reaction of benzaldehyde with propionic anhydride in the presence of sodium propionate, and recrystallized from ethyl alcohol, m.p. 81~82°C. The preparation of *p*-methoxycinnamic acid, atropic acid, and diphenylethylene, and their purification were described in a previous paper[2].

The Reaction of β-Methylcinnamic acid with Bromine and Oxygen.—β-Methylcinnamic acid (2 g.) was dissolved in 60 ml. of benzene and the solution was divided into equal portions in separate flasks, each being equipped with a small dropping funnel, and one in addition with two glass tubes for introducing oxygen into the solution. The flasks were placed in the strong sunlight, and 20 ml. of a benzene solution containing 1 g. of bromine was dropped into each flask, oxygen being passed simultaneously into one of the solutions. Here the experiment with introduction of oxygen is designated as Expt. 42-a, and the experiment without oxygen as Expt. 42-b. The color of the solution in Expt. 42-b faded in less than five minutes, while that of Expt. 42-a slowly and remained even for four hours. No evolution of hydrogen bromide was observed during the reaction in either case. In Expt. 42-a, after oxygen was passed for about 130 minutes, the solution was kept standing in the diffused daylight for 210 minutes. From the reaction mixture, 0.31 g. of crystalline substance and 0.852 g. of an oil were obtained. The oil

9) O. Simamura, S. Nomura, and M. Takahasi, unpublished work.

10) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

(0.852 g.) was brought to react with 0.5 g. of 2,4-dinitrophenylhydrazine dissolved in 40 ml. of ethyl alcohol with 1 ml. of conc. hydrochloric acid, and about 0.239 g. of a 2,4-dinitrophenylhydrazone, m.p. 220~235°C, was obtained. The chloroform solution of the dinitrophenylhydrazone was passed through a chromatographic column of alumina, giving an orange zone and a dark brown zone. Acetophenone 2,4-dinitrophenylhydrazone, m.p. 248~250°C, was obtained from the latter zone, and identified by the mixed melting point. The orange zone gave a very small amount of an unidentified substance. The crystalline product (0.31 g.) was identified with the dibromide of β-methylcinnamic acid by the mixed melting point.

From Expt. 42-b, about 1.93 g. of β-methylcinnamic acid dibromide, m.p. 128°C, was obtained, but no oily product.

In another experiment similar to Expt. 42-a, 30 ml. of a benzene solution containing 1 g. of β-methylcinnamic acid was treated, in the sunlight for 320 minutes, with oxygen and with 30 ml. of a benzene solution containing 1 g. of bromine simultaneously. The gas from the solution was passed through distilled water and then through an aqueous barium hydroxide solution. The distilled water then gave a positive Schiff test, indicating the formation of a water-soluble aldehyde. When the benzene solution was washed with 10 ml. of distilled water, the aqueous layer gave positive reactions in Schiff test, with 2,4-dinitrophenylhydrazine, and with dimedone. An alcohol solution of dimedone gave a very small amount of a crystalline substance, m.p. 195~200°C, but its identification was unsuccessful. Barium carbonate precipitated from the aqueous barium hydroxide during the reaction weighed 0.707 g. (0.0031 mol.).

The Influence of Oxygen on the Reaction of Other Ethenoid Compounds with Bromine.—To a solution of 4 g. of cinnamic acid in 40 ml. of benzene, 30 ml. of a benzene solution containing 4.7 g. of bromine was added dropwise with passage of oxygen in the sunlight for 125 minutes. The color of bromine disappeared in about one hour. The gas from the solution was passed through distilled water and then through a barium hydroxide solution, but no barium carbonate was formed in the barium hydroxide solution, and neither the bromide ion nor a carbonyl compound was found in the distilled water. From the benzene solution about 5.9 g. of crystalline cinnamic acid dibromide precipitated, and on evaporation of the mother liquor 1 g. of slightly oil-stained crystals of cinnamic acid dibromide were further obtained.

p-Methoxycinnamic acid (1 g.) was dissolved in 60 ml. of carbon tetrachloride, and the solution was divided into two flasks. Into each flask 0.28 g. of bromine dissolved in 20 ml. of carbon tetrachloride was added in the sunlight, oxygen being passed into one of the solutions. The color of bromine faded nearly at the same rate in both solutions, and no remarkable inhibition by oxygen from addition of bromine to the ethenoid compound was observed. Hydrogen bromide was not evolved in the course of reaction, and it was suggested that addition of bromine to the double bond took place more predominantly than nuclear substitution.

The same experimental procedure as above was followed in the case of atropic acid and diphenylethylene. From atropic acid, only atropic acid dibromide, m.p. 115~116°C, was obtained either with or without introduction of oxygen. In the case of diphenylethylene, the reaction mixture was shaken with water and aqueous alkali successively. When a bromine potassium bromide solution was added to the neutral aqueous extract, tribromophenol was precipitated. Moreover, when the alkaline extract was saturated with carbon dioxide and extracted with ether, a very small amount of a phenolic substance was obtained, which showed a positive test of a phenol with ceric ammonium nitrate, and had a melting point, 63.5°C. Diphenylethylene dibromide was obtained from the both carbon tetrachloride solution on removing the solvent by distillation.

Reaction of β-Methylcinnamic Acid with Hydrogen Bromide and Oxygen.—β-Methylcinnamic acid (5.000 g.) was suspended in 70 ml. of carbon tetrachloride, and a mixture of hydrogen bromide and oxygen was passed through the suspension for 485 minutes. Here the treatment was continued longer than in the cases of the other ethenoid compounds, because preliminary experiments showed that the reaction was not completed in spite of a relatively long reaction time. A moderate amount of carbon dioxide was evolved during the whole reaction period, giving 0.608 g. of barium carbonate. About 1.5 g. of brown oil separated from the carbon tetrachloride solution. The carbon tetrachloride solution was shaken three times with 70 ml. of distilled water, and then twice with 30 ml. of 2 N aqueous sodium hydroxide. The sodium hydroxide solution was saturated with carbon dioxide, separating about 3 ml. of an oil, which was extracted with ether. Benzoyl chloride was added to 1 ml. of the oil, and the mixture was heated for some time, and poured into water. The crystalline product, after washed with aqueous sodium carbonate, was recrystallized from ethyl alcohol, giving a white crystalline substance, m.p. 102~104°C. It was identified with *p*-bromophenyl benzoate by the mixed melting point with an authentic specimen. *Anal.* Found: Br, 29.5. Calcd. for $C_{13}H_9O_2Br$: Br, 28.9%. The sodium hydroxide solution, from which the phenolic substance had been separated, was acidified with dil. sulfuric acid, and shaken twice with 100 ml. of ether. Evaporation of the ethereal solution gave about 0.321 g. of a pale yellow oil, which contained only a trace of bromine. It was presumably crude β-methylcinnamic acid, although it could not be brought to crystallization.

In another similar experiment, hydrogen bromide and oxygen were passed into a solution of β-methylcinnamic acid (10 g.) in 80 ml. of benzene for 360 minutes, and 2.2 g. of a precipitate was obtained which was identified with

β-methylcinnamic acid dibromide. Evaporation of the benzene solution gave a yellow oil. When 1.1 g. of the oil was brought to reaction with 2,4-dinitrophenylhydrazine in ethyl alcohol, a small amount of a yellow precipitate was formed. It was separated into parts soluble and insoluble in hot ethyl alcohol. The soluble part was a yellow crystalline substance, which melted at 160~164°C. The insoluble part, which weighed 0.05 g., melted at 210°C, and contained 15.8% of bromine. Further purification was unsuccessful with both substances, but the soluble substance was supposed to be 2,4-dintrophenylhydrazone of formaldehyde or of glyoxylic acid, and the insoluble to be that of α-bromoacetophenone, m.p. 214~215°C.

When hydrogen bromide was passed through a solution of 3 g. of β-methylcinnamic acid in 60 ml. of benzene without introduction of oxygen for 210 minutes, a crystalline substance, m.p. 42~80°C, was obtained, but recrystallization gave β-methylcinnamic acid only.

A reaction of α-methylcinnamic acid with hydrogen bromide and oxygen was attempted in the same way as that of β-methylcinnamic acid. No evolution of carbon dioxide was observed, and the reaction mixture gave no positive tests of a carbonyl compound, and α-methylcinnamic acid was recovered from the solution.

The Reaction of Cinnamic Acid with Hydrogen Peroxide in the Presence of Perchloric Acid.—Cinnamic acid (6.0 g.) was dissolved in 40 ml. of acetic acid, and 6 ml. of 30% hydrogen peroxide and 2 g. of 70% perchloric acid were added. Even after two days, cinnamic acid was recovered almost completely, and no formation of either a carbonyl compound or a phenol was observed. A preliminary experiment on the reaction of β-methylcinnamic acid with hydrogen peroxide in the presence of perchloric acid has shown the formation of acetophenone and glyoxylic acid.

Ultraviolet Absorption Spectra of Cinnamic Acid and its Derivatives.—The measurements of the ultraviolet absorption spectra were carried out with a Beckman type spectrophotometer. The absorption maxima of cinnamic acid, β-methylcinnamic acid and β-ethylcinnamic acid in 94% ethyl alcohol, were 273, 260 and 244 mμ, respectively, and the molecular extinction coefficients were 2.2×10^4, 1.5×10^4 and 1.0×10^4, respectively.

Summary

The action of oxygen and bromine on β-methylcinnamic acid in benzene in the sunlight at room temperature caused an oxidative cleavage of the double bond, giving acetophenone and carbon dioxide, in addition to β-methylcinnamic acid dibromide. Similar experiments with cinnamic acid, atropic acid, p-methoxycinnamic acid, gave only dibromides either with or without introduction of oxygen.

Although a complete identification of the reaction products from the reaction of hydrogen bromide and oxygen on β-methylcinnamic acid was unsuccessful, it was found that a phenolic substance and a carbonyl compound were produced and that the formation of the phenol inhibited the progress of the reaction.

On the ground of these and other results which were described in the three preceding papers, the mechanism of the reactions of hydrogen bromide, bromine, and oxygen with ethenoid compounds is discussed.

The author wishes to express his hearty thanks to Professor Y. Urushibara and Professor O. Simamura for their kind guidance and encouragement for the present work.

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The Infrared Spectra of Methoxy-, Methylmethoxy- and Methoxy Endblocked Dimethyl-polysiloxanes

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(Received June 3, 1958)

The group frequency assignments have already been given for the infrared spectra of organoalkoxypolysiloxanes, such as alkylalkoxysilanes[1] and ethoxy- and methylethoxy-polysiloxanes[2]. In this paper the infrared spectra of three types of polysiloxanes represented by A, B and C, which contain methoxy and methyl groups in various proportions, will be described.

A_n : $CH_3O[(CH_3O)_2SiO]_nCH_3$ $n=1\sim3$
B_n : $CH_3O[CH_3OSi(CH_3)O]_nCH_3$ $n=1\sim5$
C_n : $CH_3O[Si(CH_3)_2O]_nCH_3$ $n=1\sim6$

These polysiloxanes have simple structural units, and the infrared spectra seem to be explained fairly well. The vibrational spectrum of C_1 (dimethyldimethoxysilane) has been reported[3] and most of the assignments have agreed with the results which would be described in this paper. Referring to the results of this experiment and the infrared spectra of

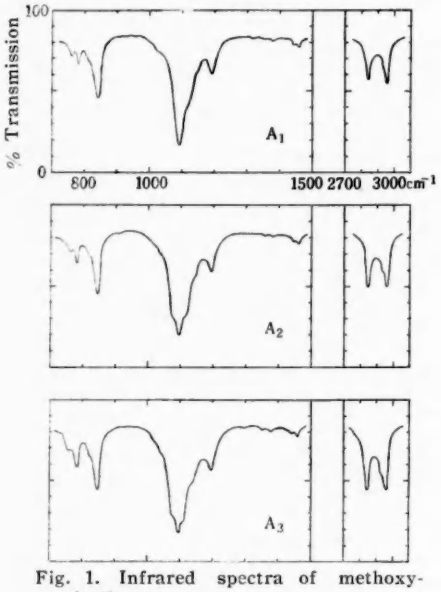

Fig. 1. Infrared spectra of methoxypolysiloxanes.
A_n: $CH_3O[(CH_3O)_2SiO]_nCH_3$, 2% in CS_2 and CCl_4.

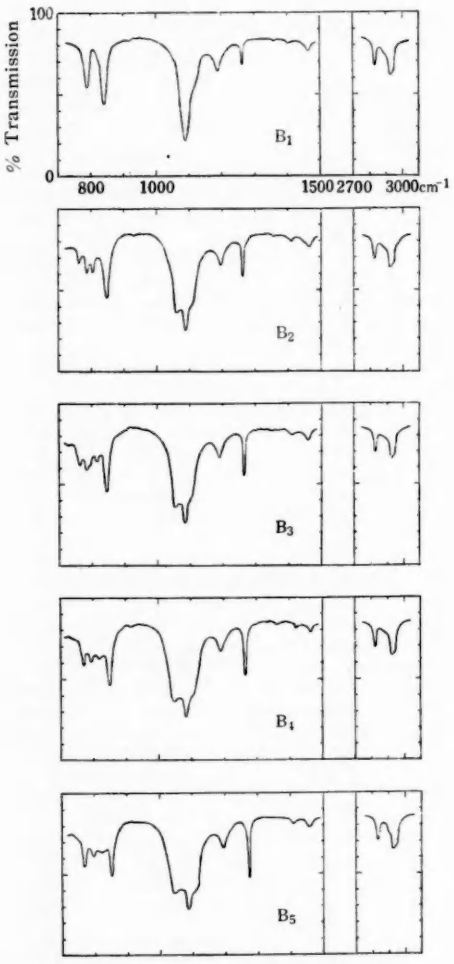

Fig. 2. Infrared spectra of methylmethoxypolysiloxanes.
B_n: $CH_3O[CH_3OSi(CH_3)O]_nCH_3$, 3% in CS_2 and CCl_4.

1) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1949**, 125.
2) R. Ōkawara, This Bulletin, **31**, 154 (1958).
3) M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 436 (1958).

dimethylpolysiloxanes[4] (represented by D), one would make the explanation of the infrared spectra of the more complicated organoalkoxypolysiloxanes.

D_n : $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$ $n=1\sim7$

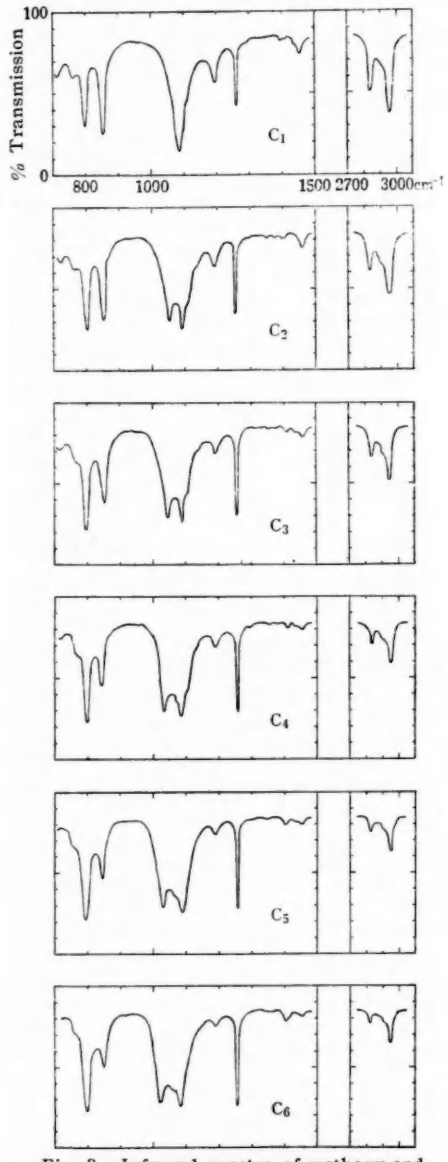

Fig. 3. Infrared spectra of methoxy endblocked dimethylpolysiloxanes.
C_n: $CH_3O[Si(CH_3)_2O]_nCH_3$, 5% in CS_2 and CCl_4.

4) N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).

Experimental

Materials.—The preparations and the properties of the members of A[5], B[6] and C[7] used in this experiment were already reported.

Measurements.—The spectra were obtained by the use of Hilger H-800 infrared spectrophotometer with a rock salt prism. Samples

TABLE I
INFRARED SPECTRA OF METHOXYPOLYSILOXANES: POSITIONS OF BANDS (in cm^{-1})

A_n		
$n=1$	$n=2$	$n=3$
760 w	762 sh	761 sh
784 m	785 m	784 m
840 s	842 s	842 s
1038 sh	1044 sh	1046 sh
—	1078 sh	1080 sh
1094 vs	1095 vs	1095 vs
1112 sh	1112 sh	1112 sh
—	1143 sh	1144 sh
1195 m	1195 m	1196 m
1352 vw	1350 vw	1351 vw
1381 w	1381 w	1381 w
1444 w	1443 w	1443 w
1458 w	1459 w	1459 w
2350 br	2332 br	2321 w
—	—	2361 w
2847 m	2848 m	2848 s
—	2943 sh	2941 sh
2965 m	2968 m	2967 s

TABLE II
INFRARED SPECTRA OF METHYLMETHOXYPOLYSILOXANES: POSITIONS OF BANDS (in cm^{-1})

B_n				
$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
—	767 m	767 m	769 m	769 m
790 m	790 m	790 m	791 w	792 w
—	808 m	818 m	821 w	822 w
845 m	847 m	848 m	850 m	850 m
—	1066 m	1051 m	1045 m	1041 m
1089 s	1088 s	1087 s	1085 s	1086 s
1110 sh	1108 sh	1109 sh	1110 sh	1112 sh
1192 m	1192 m	1193 m	1192 m	1194 m
1267 m	1266 m	1267 m	1267 m	1268 m
1402 vw	1404 vw	1403 vw	1402 vw	1405 vw
1459 w	1458 w	1457 w	1457 w	1458 w
2333 br	2342 br	2343 br	2344 br	2338 br
2825 m	2824 m	2823 m	2823 m	2825 m
2931 m	2930 m	2931 m	2930 m	2932 m
2953 sh	2951 sh	2953 sh	2953 sh	2953 sh

5) T. Tanaka and T. Watase, This Bulletin, **28**, 258 (1955).
6) T. Tanaka, A. Tasaka and R. Ōkawara, *Technol. Repts. Osaka Univ.*, **7**, 193 (1957).
7) T. Tanaka and R. Ōkawara, This Bulletin, **28**, 364 (1955).

TABLE III
INFRARED SPECTRA OF METHOXY ENDBLOCKED DIMETHYLPOLYSILOXANES: POSITIONS OF BANDS (in cm^{-1})

	C_n					
$n=1$*	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
730 s	713 w	720 w	716 vw	715 vw	—	—
	761 w	761 w	762 sh	761 sh	762 sh	761 sh
797 s	797 s	798 s	799 s	798 s	799 s	798 s
849 vs	855 s	853 s	851 s	847 s	849 m	850 m
998 vw	—	—	—	—	—	—
—	—	1055 s	1045 s	1036 s	1028 s	1021 s
1089 vs	1083 s	1091 s	1092 s	1092 s	1091 s	1092 s
—	—	1112 sh	1113 sh	1115 sh	—	—
1160 sh	—	—	—	—	—	—
1188 m	1190 m	1189 m	1191 w	1190 w	1190 w	1189 w
1258 m	1258 m	1261 s	1263 s	1263 s	1262 s	1262 s
1295 sh	—	1296 vw	1298 sh	1298 vw	—	—
1340 w	1343 vw	1343 vw	1342 vw	—	—	—
1399 sh	1399 w	1403 w	1403 w	1405 w	1405 w	1406 w
—	—	—	—	1435 sh	1439 sh	1443 sh
1456 s	1460 m	1458 m	1459 w	1458 w	1457 vw	1460 vw
—	—	2342 br	2342 br	2333 br	2316 w	2323 w
					2358 sh	2355 w
—	2830 m	2829 m	2827 m	2825 w	2826 w	2821 w
—	—	2906 sh	2906 sh	2907 sh	2906 sh	2908 sh
—	2947 s	2960 s	2956 s	2955 m	2953 m	2953 m

* M. Hayashi, *loc. cit.*[3]

were observed in this experiment both as a solution in carbon disulfide for the range 700 to 1500 cm^{-1} and in carbon tetrachloride from 1250 to 3500 cm^{-1}, and as pure liquid. The concentration of each solution was 2, 3 and 5% for A, B and C, respectively. The celles were 0.03 mm. thick in the case of the solution and less than 0.01 mm. in the case of pure liquids. No appreciable difference was observed between the two cases.

In order to compare the relative intensity approximately, the absorption of the compounds belonging to the same series have been recorded on the same chart, keeping the conditions as similar as possible. The spectra and the positions of the absorption bands obtained are presented in Figs. 1—3 and Tables I—III, respectively.

Discussion of the Results

All the compounds of A, B and C show two absorption peaks in the region 2800～3000 cm^{-1}. The members of A have a kind of methyl group attached to oxygen atom, so the two bands near 2847 and 2965 cm^{-1} are assigned to the symmetric and non-symmetric stretching vibration of (O—)CH_3 group*, respectively. These bands are also observed in B and C; the intensities decrease with the decreasing concentration of methoxy group as the polymer sizes increase, and this behavior is distinct in C. Considering this behavior and fairly weak intensity of C—H stretching band in (Si—)CH_3 group* the bands near 2825 and 2930 cm^{-1} in B and near 2825 and 2955 cm^{-1} in C are attributed to the symmetric and the non-symmetric C—H stretching vibration arising mainly from (O—)CH_3 group, respectively**. Thus the band associated with (O—)CH_3 group appears on the low frequency side of the CH absorption in (C—)CH_3 group, and this fact has been observed by Henbest et al.[8] The shoulders near 2953 cm^{-1} in B and near 2906 cm^{-1} in C would be due to the non-symmetric and symmetric C—H stretching modes of (Si—)CH_3 group in each series, respectively.

In B and C, the band near 1460 cm^{-1} decreases in strength with increasing polymer size, and that near 1400 cm^{-1} has the reverse tendency. Accordingly, the

* Represent the methyl group attached to oxygen atom.

8) H. B. Henbest, G. D. Meakins, B. Nicholls and A. A. Wagland, *J. Chem. Soc.*, **1957**, 1462.

* It has been reported[4] that the intensity of the C-H stretching band in (Si-)CH_3 was the order of one-third to one-fourth that in (C-)CH_3.

** As the concentration of O-CH_3 group is considerably small compared with that of Si-CH_3 group in the comparative higher members of C, the bands near 2925 and 2955 cm^{-1} would not always be due to the C-H stretching mode in (O-)CH_3 group.

former band is attributed to the methyl deformation vibration in O—CH_3 group referring to the wave number of that found in dimethylether (1466 cm^{-1})[9], and the latter to the methyl deformation vibration in Si—CH_3 group as already assigned[3,10].

The sharp intense band near 1260 cm^{-1} in B and C has been known to be the characteristic absorption of Si—CH_3 group. Some different assignments have been made to this band, that is, the rocking vibration[4], symmetrical deformation vibration[11] and γ-(CH) vibration[12] of (Si—)CH_3 group. In this investigation, it could not be decided what kinds of mode give this band, but considering the question from the relation between the position of methyl symmetrical deformation frequency and the electronegativity of atom, to which methyl group attaches*, the band near 1260 cm^{-1} would arise from (Si—)CH_3 symmetrical deformation mode.

The band near 1190 cm^{-1} is observed in all the members of A, B and C, and in the latter its intensity decreases with increasing polymer size. Diethyldimethoxysilane and ethyltrimethoxysilane show this band at 1189 and 1192 cm^{-1}, respectively[1], but no band is found near this wave number in D[4], and alkylalkoxy-silanes[1,3] and -polysiloxanes[2] not having methoxy group**. Therefore, the 1190 cm^{-1} band is clearly associated with O—CH_3 group, and referring to the wave number of methyl rocking vibration in dimethylether (1180 cm^{-1})[9], this band is considered to be the rocking vibration of (O—)CH_3 group. The wave number of the band associated with $Si(OCH_3)_n$ group is an approximately constant one and is larger than that of C—OCH_3 group, and the band in the region of 1189~1196 cm^{-1} is considered to be the characteristic frequency of Si—OCH_3 group.

In A, B and C, a common strong band appears near 1090 cm^{-1} which may be connected with the Si—O—C linkage*. Referring to the infrared spectra of dimethylether**, this band would be associated with $\overrightarrow{Si}—\overleftarrow{O}—\overrightarrow{C}$ stretching vibration†. The common band is also observed as a shoulder in the high-frequency side of the band near 1090 cm^{-1}, except C_1, C_5 and C_6. This band will probably correspond to the band near 1110 cm^{-1} observed in ethoxy- and methylethoxy-polysiloxanes[2].

Except in the case of the first members in each series, other bands having fairly strong intensity are observed at 1080 cm^{-1} in A, 1066~1041 cm^{-1} in B and 1055~1021 cm^{-1} in C. These bands in B and C decrease in wave number with increasing polymer size. This tendency has been observed in D[4] and in methylethoxypolysiloxanes[2], and these bands are clearly connected with Si—O stretching vibration in Si—O—Si linkage. The corresponding band at 1080 cm^{-1} in A would be observed as a shoulder on account of the extremely strong band at 1090 cm^{-1}. Thus, in the compounds except in the case of the first

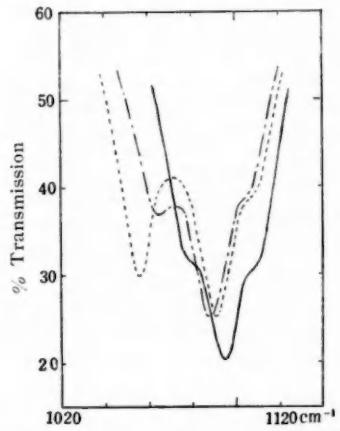

Fig. 4. Spectral sequence corresponding to the structural unit sequence of SiO_4, SiO_3C and SiO_2C_2.
——— $CH_3O[(CH_3O)_2SiO]_2CH_3$
— - — $CH_3O[CH_3OSi(CH_3)O]_2CH_3$
------ $CH_3O[Si(CH_3)_2O]_2CH_3$

9) G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, New York (1949) p. 353.
10) M. Sakiyama, This Bulletin, **31**, 67 (1958).
11) C. Y. Young, J. S. Koehler and D. S. McKinney, *J. Am. Chem. Soc.*, **69**, 1910 (1947).
12) D. H. Rank, B. D. Saksena and E. R. Shull, *Discuss. Farad. Soc.*, **9**, 187 (1950).

* For example, F-CH_3 1475, O-CH_3 1466 (in dimethylether), N-CH_3 1418 (in methylamine), Cl-CH_3 1355, S-CH_3 1323 and P-CH_3 1280 cm^{-1}; L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co. London (1954) p. 24.

** For example, in ethoxypolysiloxanes the corresponding band appears near 1160 cm^{-1}, and has been considered to be the characteristic frequency of Si-OC_2H_5 group[2].

* The band near 1090 cm^{-1} would be also connected with Si-O-Si linkage as later described.

** The band due to the non-symmetric stretching vibration of C-O-C linkage appears at 1110 cm^{-1} [9].

† $\overrightarrow{Si}-\overleftarrow{O}-\overrightarrow{C}$ stretching band may be expected to appear in the vicinity of $\overrightarrow{C}-\overleftarrow{O}-\overrightarrow{C}$ stretching band, on account of the great force constant of Si-O bond, in spite of the large mass of silicon atom.

members in each series, a spectral sequence corresponding to the structural unit sequence of SiO_4, SiO_3C and SiO_2C_2 is found for the Si—O stretching frequency as shown in Fig. 4.

In D except D_2, the further band connected with Si—O—Si linkage has been found in the region of 1070~1093 cm^{-1} [4]. The corresponding band is expected to appear in A, B and C, but it will probably be comprised in the band due to $\overrightarrow{Si}—\overleftarrow{O}—\overrightarrow{C}$ stretching. This presumption is considered from the following fact; in C, as the polymer size increases the concentration of Si—O—C linkage decreases rapidly, but the rapid decreasing in strength of 1090 cm^{-1} band is not less noticeable observed.

Some strong bands appear in the region 750~900 cm^{-1}. One of them is observed at approximately constant wave number near 850 cm^{-1} in A, B and C, but is not in D. The intensity of this band decreases with increasing polymer size in B and C, especially in the latter. So there is no doubt that the band is associated with the grouping $Si(OCH_3)_n$ (n=1~4), and is not considered to be due to the rocking vibration of (Si—)CH_3 group which has been reported by Hayashi[3]. Similar behavior to the above has been observed in the 840 cm^{-1} band of ethoxy endblocked dimethylpolysiloxanes[2]. Referring to the spectra of dimethylether*, this band will probably be associated with the $\overleftarrow{Si}—O—\overrightarrow{C}$ vibration.

It has been known that the bands near 790 cm^{-1} in B and near 800 cm^{-1} in C have been associated with $SiCH_3$ and $Si(CH_3)_2$ groups, respectively[1,4]. In B except B_1, the absorption bands appear in the frequency on both sides of the 790 cm^{-1} band; the one at the lower wave number increases in strength as well as shifting to the side of less wave number, and the other becomes broader, as the polymer size increases. The band at 795 cm^{-1} in A would be considered to be a harmonics of the deformation vibration band involving Si—O linkage, which has been supported to fall in 770~830 cm^{-1} region by Wright and Hunter[4].

* The band due to the symmetric stretching vibration of C-O-C linkage is observed at 940 cm^{-1} [2].

Summary

1) The infrared spectra of the lower members of methoxy-, methylmethoxy- and methoxy endblocked dimethyl-polysiloxanes have been discussed by comparing them with that of dimethylether, dimethylpolysiloxanes, and so on.

2) The characteristic absorption band of Si—OCH_3 group has appeared near 1190 cm^{-1}.

3) Except in the case of the first members of these alkoxysiloxanes, a spectral sequence corresponding to the structural unit sequence of SiO_4, SiO_3C and SiO_2C_2 has been observed in the region of 1000~1100 cm^{-1}.

The author wishes to express his hearty thanks to Professor T. Watase and Dr. R. Ōkawara for their helpful discussion.

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SHORT COMMUNICATIONS

A New Method for Determining the Potential of the Electrocapillary Maximum by the Vibrated Dropping Mercury Electrode

Hideo IMAI, Senkichi INOUYE and Shōkichi CHAKI

(Received May 15, 1958)

The current-voltage curve of the mercuric ion was recorded with a conventional polarograph, using the vibrated dropping mercury electrode (VDME), to which an a. c. electric field is applied (cf. Fig. 1).

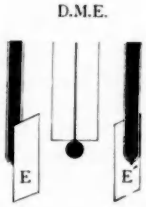

Fig. 1. The vibrated dropping mercury electrode: E, E' are the platinum plate electrodes to which the a. c. voltage is applied.

The a. c. electric field exerts a force as great as qE (q; the surface charge of the DME, E; the intensity of the a. c. electric field) on the DME, and causes the mechanical vibration of the DME. The vibration results in the increase of the limiting current of the electrolytic reduction of the mercuric ion, the convection current being superinduced on the diffusion-controlled one.

In the region of the positive polarization, the vibration gradually retards as the applied potential is shifted toward more negative potentials, corresponding to the decrease of the surface charge, and accordingly, the convection current gradually decreases. At the potential of zero charge, that is, the potential of the electrocapillary maximum, the vibration entirely ceases, and the limiting current is solely controlled by the diffusion. In the region of the negative polarization, the limiting current reincreases as the applied potential is shifted toward more negative potentials, corresponding to the increase of the surface charge. Thus, one can obtain the current-voltage curve which gives a minimum at the potential of the electrocapillary maximum, as is illustrated in Fig. 2. The more intensified is the electric field, the sharper is the "cut-in" of the minimum (cf. Fig. 2 A and B).

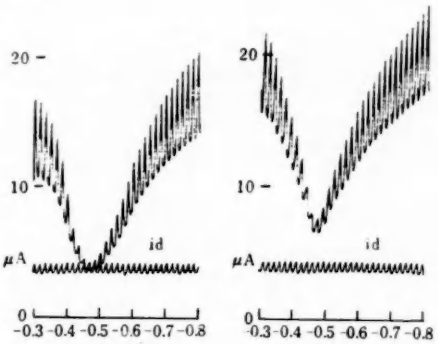

Fig. 2. The VDME current-voltage curve of $1 \cdot 10^{-3}$ M Hg^{++} in 0.1 M KCl. The a. c. frequency = 25 c. p. s. The intensity of the a. c. field = 0.55 volts/cm. (Curve A), 0.60 volts/cm. (Curve B). The mercury head = 23.5 cm. The life-time of the DME = 9.9$_4$ sec. (open circuit). The rate of mercury flow = 0.85$_5$ mg./sec. Temperature = 25°C.

The potential of the electrocapillary maximum in various solutions was evaluated by this method, and the data gave a good agreement with those given by D. C. Grahame[1]. Among the various methods of measuring the potential of the electrocapillary maximum[2], this VDME method seems to be most promising in point of the ease and rapidness of the recording, of its good reproducibility and

1) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).
2) D. C. Grahame, R. P. Larson and M. A. Poth, *J. Am. Chem. Soc.*, **71**, 2978 (1949). T. I. Popova and T. A. Kryukova, *J. physik. Chem.*, **25**, 283 (1951). J. A. V. Butler, "*Electrocapillarity*", Methuen Co. Ltd., London, (1940), p. 56.

accuracy. Moreover, this technique has the potentiality for the sensitization of the polarographic analysis as the rotated dropping mercury electrode[3] is the case.

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3) G. Charlot, "*Modern Electroanalytical Methods*", Elsevier Pub. Co., Amsterdam, (1958), I. M. Kolthoff and Y. Okinaka, p. 83 and N. Tanaka et al., p. 97.

Nuclear Magnetic Resonance Experiment of Diacetylhydrazine

By Ryuichi Shintani, Hideaki Chihara, Junkichi Itoh and Isamu Nitta

(Received May 26, 1958)

The X-ray difference electron-density contour map (D-map) of anhydrous diacetylhydrazine clearly shows peaks to be ascribed to hydrogen atoms of methyl groups as well as of amide groups[1]. This led us to the study of the proton nuclear magnetic resonance of this crystal in order to examine if the methyl groups really rest in the most stable potential minima or they are reoriented among equivalent positions.

Diacetylhydrazine was purified by repeated fractional sublimation in high vacuum, and powdered specimen was sealed in a thin glass tube in vacuo at above the dehydration temperature 82°C to assure the formation of no hydrate crystals.

The magnetic resonance was recorded with the equipment already reported elsewhere[2]. The results are given in the figures. The second moments (see Fig. 1) of the absorption at room temperature and down to −180°C are nearly constant in rough agreement with the theoretical value based on a rotating methyl group (about its three-fold symmetry axis). At liquid nitrogen temperature the second moment approaches to that corresponding to the rigid-lattice value. Therefore, the hydrogen peaks in the D-map[1] must correspond to reorienting methyl groups. It is inferred that there would be rather severe requirements to be satisfied in order for such peaks to appear in the D-map. The fact that the C–C_{Me} bond length is very short (1.48 Å) for a normal single bond may possibly be responsible for that effect.

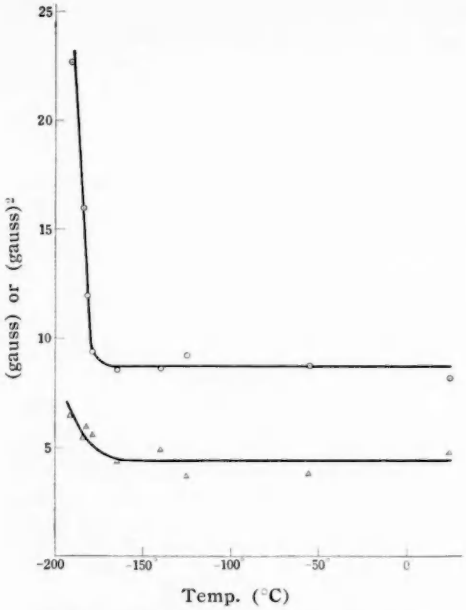

Fig. 1. The second moment and the linewidth of proton nuclear reasonance absorption of diacetylhydrazine crystals.
⊙ Second moment in gauss²
△ Width in gauss

The measurements of the spin-lattice relaxation time T_1 were then made with a hope of obtaining the barrier height hindering the internal rotation of the

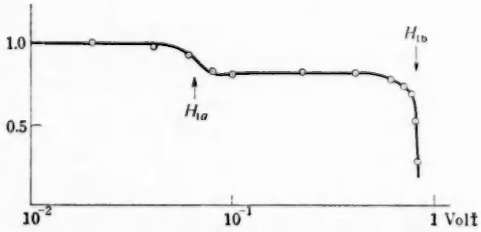

Fig. 2. A typical saturation curve at −110°C. The ordinate is in an arbitrary scale.

1) R. Shintani and I. Nitta, read before the 4th International Congress of Crystallography, July 1957 (Montreal, Canada).
2) T. Yukitoshi, H. Suga, S. Seki and J. Itoh, *J. Phys. Soc. Japan*, **12**, 506 (1957).

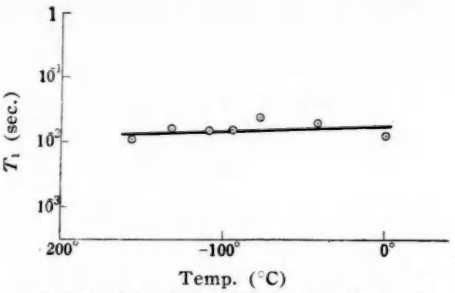

Fig. 3. The temperature dependence of the spin-lattice relaxation time T_1.

methyl groups. One of saturation curves is reproduced in Fig. 2, which has two horizontal portions with two knees at H_{1a} and H_{1b} followed by a monotonous decline. The first knee at H_{1a} was not so distinct at some other temperatures as the one reproduced here, owing to poor signal-to-noise ratio. The temperature dependence of T_1 in Fig. 3, obtained by correlating the oscillator output with the strength of the high-frequency field through calculation based on the coil dimensions and by using the portion of saturation curve at higher field than H_{1a} as the reference, was rather unusual in that T_1 (of the order of magnitude 2×10^{-2} sec.) was almost independent of the change in temperature. Although the magnitude of the T_1 values may be considered as reasonable for this type of crystal, it seems that the invariance of T_1 can hardly be accounted for by reorientation of methyl groups as dominating mechanism of nuclear relaxation. A trial of detecting possibly-present paramagnetic ingredients in the specimen by the electron-spin resonance was not successful[3]. Paramagnetic species does not exist, if any, in a greater concentration than 10^{-5} in mole fraction. Incidentally, it was found that the absorption line-width, measured by the separation between points of maximum positive and negative slope, also depends on the strength of the high-frequency field as is shown in Fig. 4. This type of experiment was conducted only at −183°C, but its precision was much greater than the measurements of the saturation curves. The absorption narrowed at an oscillator output coinciding approximately with H_{1a}. This means that the component of absorption having larger width is more readily saturated.

3) The authors are grateful to Mr. K. Morigaki of Department of Physics, Osaka University for examination of the electron spin resonance of diacetylhydrazine.

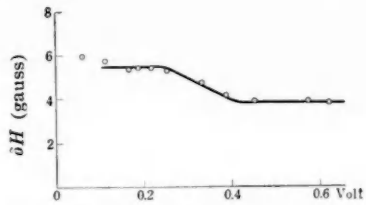

Fig. 4. Change of line-width with the strength of high-frequency field at −183°C.

An explanation was seeked which can account for the entire observation with consistency, but the present data seem to be insufficient to permit it. The role of the amide hydrogen atoms is not quite evident and substitution of deuterium for the hydrogen will provide us with further information. Inasmuch as we have no further attempt to attack this problem, satisfactory elucidation of the mechanism of the nuclear resonance in this crystal will be deferred until more data are accumulated as to the behavior of analogous substances.

Two of us (R. S. and H. C.) wish to thank Mr. Y. Yamagata of Osaka University for suggestions on the experimental details.

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Intramolecular Interaction between Hydroxyl Group and Aromatic Nucleus in 2-Hydroxy-4- or 4'-nitrobiphenyl

By Michinori Ōki, Hiizu Iwamura and Yoshiyuki Urushibara

(Received June 3, 1958)

In the course of a study on the ultraviolet spectra of biphenyl derivatives, the authors observed a phenomenon[1] possibly interpretable from the intermolecular

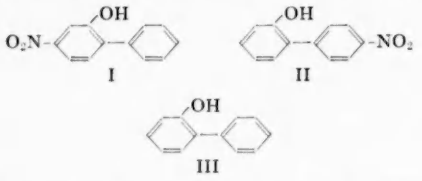
1) For example, 2-methyl-4-nitrobiphenyl shows an ultraviolet absorption maximum at a shorter wave length than 2-methyl-4'-nitrobiphenyl does. A paper on this phenomenon was presented at the Eleventh Annual Meeting of this Society, April, 1958, in Tokyo, but no full explanation has been obtained so far.

TABLE I

INFRARED SPECTRA OF 2-HYDROXY-4-NITROBIPHENYL (I) AND 2-HYDROXY-4'-NITROBIPHENYL (II)

Compound	Temp. (°C)	Hydroxyl	ν_{max} (cm^{-1})	$\Delta\nu_{1/2}^{0}$ (cm^{-1})	$A\times10^{-4}$ $mole^{-1}\cdot liter\cdot cm^{-2}$	$\Delta\nu_{max}$ (cm^{-1})
I	26.5	interacted	3553.8	19.4	1.703	44.0
		free	3597.8	19.6	0.233	
II	23.5	interacted	3579.6	17.6	0.765	21.4
		free	3601.0	17.2	0.787	

interaction involving a participation of the aromatic nucleus, which led the authors to study the absorption spectra of 2-hydroxy-4-nitrobiphenyl (I)[2], m.p. 103~105°C, and 4'-nitro-isomer (II)[3], m. p. 123~124°C.



Wulf[4] observed two O–H stretching bands in the first overtone region in 2-hydroxybiphenyl (III), attributing them to *cis* and *trans* isomerism. Barnard et al.[5] also observed two bands in 3μ region in cumene α-hydroperoxide. In view of recent studies on the intermolecular interaction between the hydroxyl group and the aromatic nucleus, these phenomena are undoubtedly caused by the intramolecular interaction between the hydroxyl group and the π-electrons of the aromatic nucleus. While the present study was in progress, Trifan and his coworkers[6] reported that they also observed two O–H stretching bands in α-hydroxyethylferrocene and β-phenethyl alcohol.

It can naturally be expected that introduction of a nitro group into compound III will either enhance or suppress the interaction by the electron drawing power of the nitro group and compounds I and II will be the two extremes as far as the positions 4 and 4' concern on the basis of Hammett's σ values.

The infrared absorption was measured with a Perkin Elmer Model 112-G Double Pass High Precision Grating Infrared Spectrometer, the spectral slit width being 0.82 cm^{-1} in this region. Eastman-Kodak spectro grade carbon tetrachloride was used as a solvent without further treatment. A quartz absorption cell of 2 cm. length was used with a ca. 0.001 mol./l. solution. The temperature varied from 25° to 65°C. The integrated intensity was calculated from the equation given by Ramsay[7], four parameters a_1, b_1, c_2 and b_2 being used for the two bands. Examples of the results are shown in Table I.

Energy differences between free and interacted hydroxyl groups calculated from the values at various temperatures are 2.5±0.2 and 0.93±0.03 kcal./mol. for compounds I and II, respectively, and are in good agreement with the expectation. There may exist a relation between ΔE and $\Delta\nu$ or the integrated intensities of free and interacted forms, but we can not comment about this until further examples are studied.

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2) C. Finzi and A. Mangini, *Gazz. chim. ital.*, **62**, 664 (1932); *Chem. Abst.*, **27**, 77 (1933).
3) W. G. Christiansen and S. E. Harris, *J. Am. Pharm. Assoc.*, **22**, 723 (1933); *Chem. Abst.*, **29**, 4382 (1935).
4) O. R. Wulf, *J. Am. Chem. Soc.*, **58**, 2290 (1933).
5) D. Barnard, K. R. Hargrave and G. M. G. Higgins, *J. Chem. Soc.*, **1956**, 2845.
6) D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **79**, 6566 (1957).
7) D. A. Ramsay, ibid., **74**, 72 (1952).

Gas Chromatographic Separation of Hydrogen Isotopes D_2 and HD

By Sumio OHKOSHI, Yuzaburo FUJITA and Takao KWAN

(Received June 12, 1958)

A simple gas adsorption chromatographic apparatus was constructed by us[1] with materials readily available in this physicochemical laboratory. The apparatus had the advantage of operating the adsorption column at any desired temperature and so far was used as a tool for analyses of

1) S. Ohkoshi, Y. Fujita and T. Kwan. *Catalyst*, **15**, 1 (1958).

low boiling gases, however with potential purpose of separating and analyzing hydrogen isotopes D_2, HD and H_2. The latter investigation was now performed and led to a certain satisfactory aspect which will be described below.

Experience[1] has shown that the efficiency of gas chromatographic separation largely depends on the nature of column packings and on the temperature of the column. Experiments were therefore conducted primarily to find out most favorable column packing and temperature. As a result Pyrex glass U-tube of 80 cm. long and 0.3 cm. internal diameter was employed as a column and filled with "molecular sieve 5 A" due to Linde Air Co. New Jersey, the column being immersed, when working, in a liquid nitrogen bath.

Two hydrogen isotope samples were investigated for the purpose; one was pure deuterium (>99.5%) supplied by Stuart Oxygen Co. San Francisco and the other was prepared by contacting a mixture of pure deuterium and ordinary hydrogen in a ratio of 1.8 : 1.0 with a reduced nickel powder kept at 100°C to reach isotopic exchange equilibrium. Ordinary hydrogen from cylinder was used as a carrier gas, its flow rate being 70 ml. per min. A known amount of the sample gas under reduced pressure was introduced in a manner as described previously[1] into the stream of the carrier from the sample tube of known volume which was connected to sample reservoirs, mercury manometer and then to vacuum line. The thermal conductivity cell with thermistor was used to detect hydrogen isotopes. Now, under such experimental circumstances there appeared two distinct elution peaks, when a mixture sample after equilibration was introduced, which were almost perfectly separated with each other. In Fig. 1 is shown such a chromatogram which was recorded however by a commercial set of the gas chromatography-Shimazu GC-1A, No. 58035* recently furnished in this laboratory.

As shown in Fig. 1, it is apparent that the retention time for pure deuterium is coincident with that of the second peak

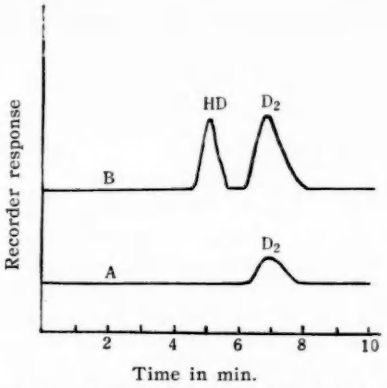

Fig. 1. Chromatogram of hydrogen isotopes. A: Pure deuterium. B: A mixture of D_2, HD and H_2 after equilibration at 100°C.

of the chromatogram for the mixture sample. Since ordinary hydrogen was employed as the carrier gas, H_2 in the mixture should not appear in the chromatogram. The first peak, therefore, should be identified as HD. It is interesting to note that coiled Pyrex column of the same length tended to have a slightly lower efficiency to separate hydrogen isotopes.

Attempts were made by Glueckauf and Kitt[2] to obtain pure deuterium from a mixture of D_2 and H_2 by using a column filled with palladium black-asbestos and kept between 0 and 100°C. Similar investigation was carried out by Tamaru[3] who used palladium-on-Celite as column packing. So far as we are aware, there is no report concerning complete separation of D_2 and HD by means of the gas chromatographic technique. The present finding surely proves the gas chromatography to be a new tool for quantitative as well as qualitative analysis of hydrogen isotopes; it is possible to proceed to determination of the amount of constituents D_2, HD and H_2 for a given volume of the mixture, if appropriate calibration data are beforehand arranged. Experiments are continuing along this line and will soon be published.

Research Institute for Catalysis and Chemistry Department, Hokkaido University, Sapporo, Japan

* The function of this instrument is essencially the same with that constructed in our laboratory except that the thermal conductivity cell is equipped with coiled tungsten heater wires. The advantage of the commercial set may be the equipping of a self-recording system which we lack in ours. Its disadvantage, on the other hand, is a certain limitation in operating the column temperature, viz., it is designed primarily for above-room-temperature. The only modification was that the original stainless steel column arranged horizontally had to be replaced by a vertical glass U-tube.

2) E. Glueckauf and G. P. Kitt, "Vapor Phase Chromatography", Butterworths Scientific Publications, London (1957) p. 422

3) K. Tamaru, Private communication.

*Gas Chromatography as a New Tool for Analyses of Hydrogen Isotopes**

By Sumio Ohkoshi, Shoko Tenma, Yuzaburo Fujita and Takao Kwan

(Received July 5, 1958)

A mixture of hydrogen isotopes could completely be separated[1,2] by use of a technique of the gas adsorption chromatography, when the adsorption column was filled with "molecular sieves 5A"** and cooled in a liquid-nitrogen bath. Preliminary experiments were then carried out with special interest in applying the gas chromatography as a new tool for quantitative analyses of these hydrogen molecular species. In the followings a record of these will be presented.

Ordinary hydrogen and pure deuterium*** (>99.5%) were mixed in a ratio of 1.0 : 2.0 and reserved in a glass flask (sample I). A portion of this mixture was brought into contact with platinum-wire catalyst kept at 300°C overnight to reach isotopic exchange equilibrium (sample II). Chromatograms were obtained alternatively on the sample I and II by varying the sample volume. As the amount of deuterium is known in the sample I, the relation between deuterium amounts and peak heights or any other peak feature can be determined. Thus, it was found that a linear relationship, passing through the origin, holds between deuterium amounts and peak heights. The amount of deuterium in the sample II can now be estimated from the observed peak height by use of the calibration line just determined.

The amount of D_2 for a given volume of the sample II was found always smaller, as expected, than that before equilibration. Assuming that this difference in the deuterium content is due to the formation of HD and therefore corresponds to one-half of the amount of HD formed during the equilibration reaction, the amount of HD in the sample II was evaluated. Such a datum for HD is given in the Table I together with that of D_2 calculated according to the calibration line. The amount of H_2 in the sample II must now be equal to the total volume of the sample minus the sum of D_2 and HD.

In view of the rapid chemisorption and desorption of hydrogen on platinum catalyst at 300°C,[3] the hydrogen molecular species D_2, HD and H_2 in the sample II may well be expected to be in complete exchange equilibrium. In the last column of the table is shown the equilibrium constant K of the reaction as estimated from the data illustrated there.

Very slight inaccuracies in the deuterium amount of the sample II do affect the values for HD, H_2 and hence, K in the method of analysis used here. Thus, an error of about ±5% is anticipated for the value of K. The discrepancy between the observed K, 3.79, and the calculated one, 3.69[4] at a temperature of 300°C should therefore be convincing or the agreement is satisfactory.

It is concluded that the gas chromatographic techniques are convenient and powerful to analyze the amount of hydrogen molecular species D_2, HD and H_2 for both qualitative and quantitative purposes. The mass spectrometric method so far used for such purposes may be replaced to a certain extent by the gas chromatographic method.

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Table I

Amounts of hydrogen molecular species D_2, HD and H_2 before (I) and after (II) equilibration on platinum at 300°C.

Run	Isotope sample	Total volume of sample, ml. 20°C	Vol. of components, ml. 20°C			Equilibrium constant $K=[HD]^2/[H_2][D_2]$
			D_2	HD	H_2	
1	I	1.51	1.01	0.0	0.50	
2	II	1.21	0.540	0.532	0.138	3.79
3	I	0.947	0.632	0.0	0.315	

* Presented by T. Kwan before the Meeting of the Japan Society for Analytical Chemistry, Hokkaido on June 28, 1958.

1) S. Ohkoshi, Y. Fujita and T. Kwan, *Catalyst*, **15**, 1 (1958).

2) S. Ohkoshi, Y. Fujita and T. Kwan, This Bulletin, **31**, 770 (1958).

** Linde Air Products Co., New Jersey, U. S. A.

*** Stuart Oxygen Co., San Francisco, U. S. A.

3) T. Kwan, *J. Res. Inst. Catalysis, Hokkaido University*, **2**, 81 (1949); *Advances in Catalysis*, **6**, 67 (1954) (Academic Press. New York).

4) H. C. Urey, *J. Chem. Soc.*, **1947**, 562.

Enrichment of Deuterium by Low Temperature Gas Adsorption Chromatography

By Sumio Ohkoshi, Shoko Tenma, Yuzaburo Fujita and Takao Kwan

(Received August 15, 1958)

In 1934 Taylor et al.[1] found that the separation of hydrogen isotopes H_2, HD and D_2 is effective by the use of the desorption of these molecules from the surface of active charcoal kept at liquid air temperature. Accordingly, the composition of the hydrogen sample desorbed during the last stage showed an increase in the amount of HD and D_2 compared with that of the initial gas. In recent years, Barrer[2] and others have shown that dehydrated zeolite gives rise to efficient adsorption characteristics in many respects. The finding has led to an idea of "molecular sieve" which was now made available by Linde Air Products Co. New Jersey in commercial scale. We employed the molecular sieve as column packing of the gas adsorption chromatography and were able to separate HD and D_2 at a column temperature of liquid nitrogen[3]. Further investigtions by us[4] proved that the gas chromatographic technique is useful for the analyses of H_2, HD and D_2.

In view of the remarkable efficiency with which HD and D_2 are separated chromatographically through a column, filled with molecular sieve 5A and immersed in a liquid nitrogen bath, attempts were made to enrich deuterium by passage of a mixture of hydrogen isotopes such a column. The result, though of preliminary nature as yet, seemed to be noteworthy and will be communicated here.

The apparatus[5] used for the investigation of hydrogenation kinetics was used without any particular modification for the present purpose. A glass flask of ca. 1 liter volume containing 330 mmHg hydrogen isotope mixture was connected to a U-shaped glass column filled with molecular sieve 5A, to a Töpler pump and then to a sample vessel of ca. 10 cc. volume. The column was of 30 cm. in length and 0.6 cm. in internal diameter. Mercury manometers were equipped between the sample flask and the adsorption column as well as between the column and the Töpler pump to read the pressure of hydrogen sample before and after passage through the column.

The experimental procedure was as follows: the apparatus was first evacuated at room temperature and then the column was immersed into a liquid nitrogen bath. A mixture of hydrogen isotopes was introduced, by opening the cock of the flask, into the column. Rapid adsorption of hydrogen on the packing took place with residual pressure of about 30 mmHg. The rate of passage of hydrogen through the column was however not so fast; it took more than 5 minutes to reach a few mmHg in a space between the column and the Töpler pump. The hydrogen once passed through the column was continuously collected by means of the Töpler pump, and a small portion of the collected hydrogen was analysed for the isotopic composition by the gas chromatographic technique developed by us[5].

It was found that the hydrogen sample collected initially contained neither HD nor D_2. The amount of HD, however, increased gradually with increase of the volume of the hydrogen passed, and finally D_2 was found to appear in the sample gas when the liquid nitrogen bath was removed from the column and adsorbed hydrogen sample was collected back into the original flask. The pressure of the hydrogen sample in the flask was 140 mmHg showing that about 60% of the hydrogen sample was passed through the column.

In Table I is shown the composition of hydrogen isotopes H_2, HD and D_2 before and after the passage.

Table I

Enrichment of deuterium by the low temperature gas adsorption chromatography

	Total vol. ml. 20°C	H_2		HD		D_2	
		ml.	%	ml.	%	ml.	%
Isotope sample before passage	435	196	45	100	23	139	32
Isotope sample after passage	184	20	11	32	17	132	72
Isotope sample* passed through	251	176	70	68	27	7	3

* Calculated from the volume of hydrogen sample before and after the passage.

The separation factor f of the hydrogen isotopes H_2 and D_2 is defined as

$$f = \frac{n'_{D2}}{n'_{H2}} \Big/ \frac{n_{D2}}{n_{H2}}$$

where (n_{H2}, n_{D2}) and (n'_{H2}, n'_{D2}) are the concentrations of H_2 and D_2 before and

1) A. J. Gould, W. Breakney and H. S. Taylor, *J. Chem. Phys.*, **2**, 362 (1934).
2) R. M. Barrer, ibid., **47**, 82 (1950).
3) S. Ohkoshi, Y. Fujita and T. Kwan, This Bultin, **31**, 770 (1958).
4) S. Ohkoshi, S. Tenma, Y. Fujita and T. Kwan, ibid., **31**, 772 (1958).
5) S. Tenma and T. Kwan, *Catalyst*, **15**, 11 (1958).

after the passage respectively. From the data in the table the separation factor was found to be 92.

It is concluded that the low temperature gas adsorption chromatography is extremely efficient and very simple to enrich deuterium from a mixture of H_2, HD and D_2. Experiments are to be conducted to enrich deuterium from hydrogen isotope mixture of various concentrations including ordinary hydrogen.

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Magnetic Susceptibilities of Aromatic Compounds Dissolved in Sulfuric Acid

By Yoshio MATSUNAGA

(Received June 9, 1958)

Various authors have reported that a number of aromatic compounds dissolved in concentrated sulfuric acid exhibit electron spin resonance absorption. In the case of bianthraquinon and perylene, the fraction of the radical form has been estimated as ten percent or more[1,2]. On the other hand, the static susceptibility measurement is available only for bianthraquinone, and this result does not support such a high fraction of the radical form[3].

In Table I the molar susceptibilities are presented, observed for ten compounds dissolved in 96% sulfuric acid together with the values in the solid state. The concentration of the compounds in sulfuric acid ranged from four to nine percent. The values for dissolved materials were calculated by the application of Wiedemann's additivity rule. The apparent molar susceptibilities of perylene and bianthraquinone in solution are undoubtedly less than those in the solid state. If we assume that the decrease of molar susceptibility is due to the partial compensation of diamagnetism by the paramagnetic contribution of the radical form and the diamagnetic contribution of the paramagnetic species is equal to that of the diamagnetic molecule, the fraction of the molecules with a single unpaired electron is given by $\Delta\chi\times10^{-6}/1270\times10^{6}$. The estimated fraction for perylene is found to be 13.2 percent. This value is only one third of that given by Yokozawa and Miyashita[2]. As Selwood and Dobres[4] pointed out in the case of triarylmethyl radicals, the disagreement may be due, at least in part, to the enhanced diamagnetic contribution of the radical form. Although Theilacker, Kortüm and Elliehausen[3] could not find any appreciable change in the diamagnetic susceptibility of bianthraquinone, our measurement shows that 4.6 percent of the molecules are in the paramagnetic state. However, our value is still about one half of that estimated by resonance absorption[1]. Anthraquinone and fluorenone were reported to be paramagnetic in sulfuric acid and the fraction of the radical form was estimated as five percent or less[1]. Our results show that the last eight compounds in Table I including anthraquinone and fluorenone do not form any radical or the fraction of the paramagnetic species is less than one percent.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF AROMATIC COMPOUNDS IN SULFURIC ACID AND IN THE SOLID STATE

Substance	Molar Suscept. in H_2SO_4	$(-\chi_M\times10^6)$ in Solid
Perylene	0± 8*	168[5]
Bianthraquinone	161±11	220[6]
Anthraquinone	103± 6	114[6]
1-Aza-anthraquinone	102± 6	109
Phenanthraquinone	102± 6	105[5]
Anthrone	122± 6	118[6]
Bianthrone	231±11	229[6]
Fluorenone	90± 5	99.4
Benzanthrone	141± 7	143[5]
Bis(anthronylidene)-ethane	232±12	232

* Estimated experimental error.

As to the nature of the paramagnetism, a triplet state[2] and a positive ion[7] were suggested for perylene and conjugated

1) J. M. Hirshon, D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **75**, 4115 (1953).
2) Y. Yokozawa and I. Miyashita, *J. Chem. Phys.*, **25**, 796 (1956).
3) W. Theilacker, G. Kortüm and H. Elliehausen, *Ber.*, **89**, 2306 (1956).
4) P. W. Selwood and R. M. Dobres, *J. Am. Chem. Soc.*, **72**, 3860 (1950).
5) H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).
6) Y. Matsunaga, ibid., **29**, 582 (1956).
7) S. I. Weissman, E. de Boer and J. J. Conrad, *J. Chem. Phys.*, **26**, 963 (1957).

acid ions[1] for anthraquinone and bianthraquinone etc. These compounds are markedly protonated in solutions of strong acids like sulfuric acid[8,9], however, it has been pointed out that protonation is not sufficient condition for radical formation[10]. As shown in this paper, the fraction of the radical form is not high, so the structure of the paramagnetic species without protonation cannot be excluded. Although we cannotdiscuss in detail the nature of the radical form based on our own data, it must be noted that the appearence of the paramagnetic species in sulfuric acid depends greatly on the structural feature of the aromatic molecule.

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8) R. A. Herbert, M. B. Goren and A. A. Vernon, *J. Am. Chem. Soc.*, **74**, 5779 (1952).
9) T. Handa, This Bulletin, **28**, 483 (1955).
10) C. MacLean and J. H. van der Waals, *J. Chem. Phys.*, **27**, 827 (1957).

Vapor Phase Catalytic Hydrogenation of Organic Compounds Using Stabilized Nickel Catalyst[1]

By Kazuo HATA, Ken-ichi WATANABE and Masaru TANAKA

(Received June 24, 1958)

It has been known for a long time that reduced nickel catalyst prepared by thermal decomposition of nickel formate is effective for hydrogenation of many organic substances. "Stabilized Nickel Catalyst" (a kind of catalyst obtained from nickel formate) has been developed and can be prepared more conveniently for practical use, and it has been reported to show excellent quality with regard to activities and stability[1].

However, investigations in catalytic hydrogenation of organic substances using the nickel catalyst mentioned above were carried out exclusively in liquid phase, and none in vapor phase has been reported. In this paper, a new study applying this catalyst to vapor-phase hydrogenation is introduced.

As a result of experiments in which some typical organic compounds were hydrogenated, it was found that hydrogenation which this catalyst was able to be carried out in vapor phase as well as in liquid phase, and the preparation of this catalyst is simpler than that of any other nickel catalyst.

Experimental Method

The hydrogenation was carried out according to the Sabatier's method[2]. The catalyst was put into a hard-glass tube and was heated up to reaction temperature with an electric furnace, while dry hydrogen was passed through the tube. After a small amount of water from the catalyst was expelled by heating, the vaporized sample together with a large excess of hydrogen was introduced into the reaction tube. The reaction products flowing out of the tube were collected into the receiver through a condenser, and were isolated by suitable methods especially by means of fractional distillation. Then each product was identified by preparing an appropriate derivative respectively.

Results

Representative results of the experiments are summarized in Table I. Styrene and acetophenone were reduced to ethylbenzene each in high yield. Benzene was completely reduced to cyclohexane, phenol to cyclohexanol with some cyclohexanone, and benzaldehyde to benzene and toluene. Nitrobenzene was mostly reduced to aniline, however, a small amount of diphenylamine and white crystals (m. p. 193~197°C) were obtained as secondary products. Benzonitrile was reduced to toluene in good yield at about 250°C, and to benzene and toluene at about 350°C[3].

From these experiments, it is proved that the effectiveness of this nickel catalyst is as good as Sabatier's reduced nickel catalyst, and that the reaction procedure is quite simplified because of the stability of the catalyst.

1) T. Yamanaka and Y. Takagi, *J. Sci. Res. Inst. Tokyo*, **51**, 168 (1957).

2) P. Sabatier, "La Catalyse en Chimie Organique", Ch. Béranger (1913).
3) M. Tanaka, K. Watanabe and K. Hata, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **76**, 1392 (1955).

TABLE I

VAPOR PHASE CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS USING STABILIZED NICKEL CATALYST

Catalyst: a) contains 28% Ni; b) contains 40% Ni, the remainder is kieselguhr

Compound	Wt. of sample (g.)	Wt. of catalyst (g.)	Temp. (°C)	Time (hr.)	Flow velocity of sample (g./min.)	Vol. of H_2 passed (l.)	Wt. of products (g.)	Products and yields (%)	
Styrene	5	20[a)]	203	1¾	0.077	12.7	5	Ethylbenzene	(98)
Benzene	5	20[b)]	182	1½	0.073	12.1	4.1	Cyclohexane	(77)
Phenol	5	20[a)]	180	2	0.063	16.0	5	Cyclohexanol Cyclohexanone	(77) (7)
Benzaldehyde	5	20[b)]	230	1⅛	0.122	9.0	3.8	Benzene Toluene	(25) (40)
Acetophenone	5	20[a)]	203	2	0.079	14.5	4.95	Ethylbenzene	(93)
Nitrobenzene	5	20[a)]	230	1½	0.091	10.2	4.85	Aniline	(66)
Benzonitrile	5	20[a)]	250	2	0.089	11.3	3.3	Toluene	(72)
Benzonitrile	6	20[a)]	354	2	0.094	12.6	3.1	Benzene Toluene	(43) (18)

The authors are indebted to Dr. Yamanaka of the Scientific Research Institute for his suggestion and offer of "Stabilized Nickel Catalyst".

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A New Type of Urushibara Nickel Catalyst

By Kazuo HATA, Shin-ichi TAIRA and Izumi MOTOYAMA

(Received June 24, 1958)

The preparation[1], the application[2] and the characteristics[3] of Urushibara nickel catalyst, prepared from nickel chloride and zinc dust, have already been reported. In this paper the procedure of preparing a new nickel catalyst, prepared from nickel chloride and aluminum grains in place of zinc dust and named Urushibara nickel BA or U-Ni-BA in abbreviation, is presented. Aluminum grains of a proper size must be used to obtain an active catalyst. Commercially available aluminum powder proved to be invalid. Using aluminum grains of 40~80 meshes, a new type of Urushibara nickel was prepared: the precipitated nickel from aqueous nickel chloride solution with such aluminum grains was digested with aqueous caustic alkali, and a new hydrogenating catalyst was obtained. This nickel catalyst proved to be very effective for hydrogenation of various organic compounds. Above all, benzene, aniline and methyl salicylate were respectively hydrogenated under a high pressure to cyclohexane, cyclohexylamine and methyl hexahydrosalicylate, these hydrogenation being unsuccessful with Urushibara nickel B or A.

A procedure for the preparation of the most active catalyst was determined from the results of hydrogenation of acetone under ordinary pressure.

Aluminum grains of 40~80 meshes (10 g.) are washed with water and treated with 50 ml. of 3% sodium hydroxide solution until the mixture becomes hot and vigorously frothy. To this mixture is added water to suppress the frothing and the upper liquor is decanted. The aluminum grains are washed well with water to remove a trace of alkali. They are transferred into a 500 ml. wide-mouthed, round-bottomed flask or beaker and warmed with a little water on a boiling water bath. To this is added 20 ml. of hot aqueous nickel chloride solution which contains 2 g. of nickel. Occasional stirring is continued until the slushy reaction mixture becomes nearly solid. The solids are crushed two or three times with hot water to remove water-soluble products. To a mixture of the solids and a little water is cautiously added with stirring 250 g. of 20% sodium hydroxide solution in several portions. As a addition of the first portion is followed by a violent reaction, good stirring and cooling with ice are necessary to prevent the contents running over. After a half

1) Y. Urushibara, This Bulletin, **25**, 280 (1952); Y. Urushibara et al., ibid., **27**, 480 (1954); Y. Urushibara et al., ibid., **28**, 446 (1955).

2) S. Nishimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 340 (1956); ibid., **78**, 1741 (1957); ibid., **79**, 56 (1958); K. Hata et al., ibid., **77**, 1405 (1956); ibid., **78**, 186 (1957); This Bulletin, **30**, 431 (1957).

3) Y. Urushibara et al., This Bulletin, **29**, 815 (1956).

part of the alkali is added during about ten minutes, the other half is added at once to the reaction mixture, which is continuously stirred until the generation of hydrogen gas ceases. The temperature of the reaction mixture should be kept below 60°C throughout this operation. After being kept for a few minutes, the upper liquor of the dark reaction mixture is carefully

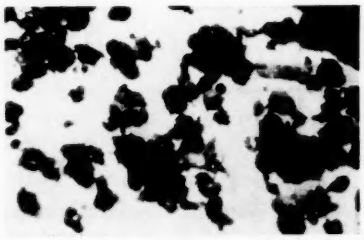

Fig. 1. Micro-photograph of Urushibara nickel BA.

decanted and the residue is washed five times with each 100 ml. of hot water and then thrice with each 50 ml. of ethanol. The solids are transferred into a hydrogenating vessel with the solvent to be used. In these stages contact with air must be avoided as far as possible. Distilled water is used for wash, and every washing is removed by decantation. In this way a very active catalyst containing about 2 g. of nickel, a small amount of aluminum and a trace of alkali is obtained.

A micro-photograph of this catalyst is given. This photograph shows that ion-exchange occurred on the surface of aluminum grains and then inner aluminum was dissolved out by the action of sodium hydroxide solution.

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Reduction of p-Nitrosodiethylaniline by Means of Activated Zinc Dust and Ammonium Chloride

By Ryoichi Uehara and Tsurahide Cho

(Received July 11, 1958)

Some reducing agents for preparation of *N*, *N*-diethyl-*p*-phenylenediamine from *p*-nitrosodiethylaniline have been reported, e. g., hydrochloric acid and stannous chloride[1], hydrochloric acid and zinc[2], and hydrochloric acid and iron[3]. Electrolytic reduction[4] and catalytic reduction[5] with Urushibara nickel are also favorable methods for the preparation. It has been found by the present authors that the reduction can be achieved very easily in methanol or ethanol by means of ammonium chloride and zinc dust activated with mercuric chloride. Reduction of nitrobenzene to phenylhydroxylamine with zinc dust and aqueous ammonium chloride is noted, but no application of this reducing agent in non-aqueous media has been reported. For the reduction of *p*-nitrosodiethylaniline, zinc dust and ammonium chloride are not effective either in water or in methanol or ethanol, but, by using zinc dust activated with mercuric chloride, the reduction takes place very smoothly in methanol or ethanol.

The procedure of this reaction is very simple. In a three-necked flask (500 cc.), fitted with a reflux condenser, a stirrer, and a dropping funnel, 40 g. (0.615 atom) of zinc dust and 50 g. (0.28 mole) of *p*-nitrosodiethylaniline are taken, and 300 cc. of methanol and 0.1 g. of mercuric chloride are added. The mixture is heated with stirring until *p*-nitrosodiethylaniline is completely dissolved and an active ebullition takes place. Then heating is stopped and 5 g. of ammonium chloride in 20 cc. of water is added drop by drop into the mixture. An active reaction occurs, and methanol boils owing to the heat of the reaction. Addition of the ammonium chloride solution is controlled so as to keep the methanol boiling gently without applying heat. After the addition of ammonium chloride, the mixture is again heated and refluxed until the original dark brown color turns pale yellow. The change of color indicates the completion of reduction of the nitroso compound to the amino compound. The solution is filtered, and the residue washed with 100 cc. of hot methanol. The filtrate and the washing are combined and evaporated in nitrogen. The residual dark oil is distilled under a reduced pressure to yield 35 g. (75.6 % of the theory) of *N*, *N*-diethyl-*p*-phenylenediamine boiling at 139~140°C/10 mm.Hg, or at 216.5°C/760 mm.Hg. Anal., N, 16.98%.

For a smooth reaction and a good yield, it is necessary to use purified *p*-nitrosodiethylaniline melting at 83~84°C, because resinous impurities in crude *p*-nitrosodiethylaniline decrease the yield of the reduction and mask the color change

1) Gattermann, "Die Praxis des Organischen Chemikers", W. de Gruyter, Berlin (1940), p. 315.
2) G. Wurster, *Ber.*, **12**, 523, 530 (1878).
3) **FIAT No. 1313** Vol. 1, p. 29, 175, 229 (1948).
4) S. Kikuchi and K. Honda, *Seisan-Kenkyu*, **2**, 267 (1950).
5) R. Uehara, unpublished data.

to indicate the end point of the reaction. *N, N*-dimethyl-*p*-phenylenediamine can be obtained from *p*-nitrosodimethylaniline in the same way.

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A Study on Anion Exchange Separation of Neptunium from Irradiated Uranium

By Fujio Ichikawa

(Received July 18, 1958)

Phillips and Jenkins[1] reported the removal of plutonium by nitrate-form anion exchanger before the analysis of fission products. According to their study, plutonium (IV) is adsorbed onto an anion exchange resin from 7.5 N nitric acid solution forming nitrate complex, but fission products and uranium pass through the column and are separated from plutonium. This method is used in a separating plant of plutonium fuel[2].

In the present communication, the adsorption of neptunium is studied in a similar way and a good separation of neptunium from fission products and uranium is found. Neptunium-239 obtained by the following way is used as a tracer.

Distribution coefficient (K_d) of neptunium is measured in systems of nitric acid and nitrate-form anion exchanger (Dowex 1, 100~200 mesh) by batch method. Figure 1 shows the acid dependence of the K_d value. In the concentration range from 1 to 10 N nitric acid, K_d value shows a linear relationship toward the concentration of nitric acid on a logarithmic scale. The maximum value is about 10^3 at 10 N nitric acid and beyond this normality the K_d value decreases suddenly.

The separation study is carried out as follows. Uranium nitrate (10 mg. U) is irradiated in J.R.R.-1 Reactor for two hours at a flux of 10^{11} neutrons/cm^2/sec.

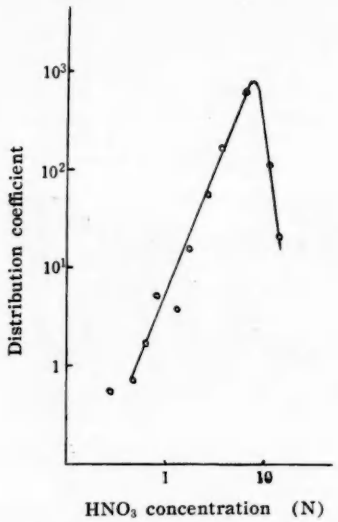

Fig. 1. The acid dependence of the distribution coefficient of Np.

The irradiated sample is dissolved in 1 N hydrochloric acid. A few mg of ascorbic acid is added to the solution in order to keep neptunium at a reduced state. After drying up the solution, the residue is taken up by 7.5 N nitric acid and then neptunium is eluted with 0.7 N nitric acid. Figure 2 shows the elution curve. According to the γ-ray spectrometry, no neptunium is found in 7.5 N nitric acid fraction. On the other hand, a spectrograph of pure ^{239}Np is obtained in 0.7 N nitric acid fraction. When the reduction procedure is omitted, the elution peaks of neptunium and fission products appear very closely in 7.5 N nitric acid and the separation is unsatisfactory.

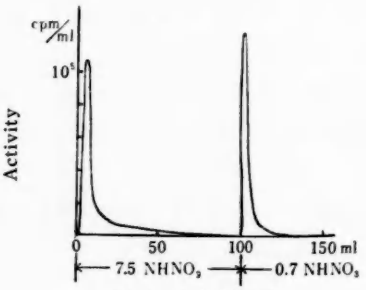

Fig. 2. The elution curve of Neptunium and fission products.

1) G. Phillips and E. N. Jenkins, *J. Inorg. Nucl. Chem.*, **4**, 220 (1957).
2) W. M. Campbell, *Nucleonics*, No. 9, 92 (1956).

From these facts, it is likely that neptunium forms a nitrate complex at a lower oxidation state in 7.5 N nitric acid and is adsorbed onto an anion exchanger, but a higher oxidation state the complex formation is very weak.

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Selective Reduction of Phospholipids with Lithium Aluminum Hydride I. Ovolecithin

By Chieko URAKAMI and Hirochika OKURA

(Received July 19, 1958)

Recently, Long and Maguire[1] have reported a method of determination of the structure of the phosphatidylcholines, involving a long series of reactions which leads to the formation of L, α-glycerophosphoric acid; Baer and Maurukas[2] have shown another method involving the diazometholysis which is simpler but applicable only to the phosphatidylserines and cephalins. Therefore, it seems desirable to find a new method which is simple in itself to be applicable even when small amounts of phosphatides are available from natural sources.

Since the mechanism of reduction by lithium aluminum hydride is generally considered to be analogous to that of Grignard reaction, the reductive cleavage of the two fatty acid ester linkages in the phosphatidylcholine molecule would take place at an equal rate and with the retention of the configuration. On the other hand, the cleavage of the linkage between the glyceryl or choline and the phosphoryl would not be so easy as the previous case since approach of the nucleophilic reagent to the P^+ to attain a coordination at the transition state may be interfered by the presence of the oxygen atoms with a high electron density around the P^+. The cleavage of the linkage between the phosphoryl and choline may, however, be effected if the mechanism proposed by Gaylord[3] is assumed to be involved. When a group such as —N—C—O is present, a quasi ring is formed by coordination of the nitrogen atom with AlH_3[4] and of the hydrogen atom of the AlH_3 with the electron pair on the oxygen atom. The adjacent carbon atom being positive in character owing to the electrostatic effect of the cationic nitrogen would then react with the hydride ion, H^-, present in the solution[4], resulting in cleavage of the C—O bond. Since a six-membered ring would be equally stable as the five-membered, as illustrated by Gaylord, this mechanism may be applicable to the case of the phosphatidylcholine molecule. In this case however, the reaction would not take place so readily as the cleavage of the fatty acid ester for the following two reasons; firstly, the weakly acidic AlH_3 must overcome the zwitterionic effect in its approach to the nitrogen atom; and secondly, the electrostatic effect would be much weaker on the β-carbon atom. Therefore, under carefully controlled reaction conditions, it may be possible to carry out the cleavages in a stepwise manner to give L, α-glycerophosphorylcholine in the first step and L, α-glycerophosphoric acid in the following. Complicated reactions may, however, occur in the last step, as demonstrated by Karrer and Jucker[5].

The sample of lecithin employed was purified according to the method described by Rhodes and Lea[6] and Hanahan, et. al.[7]

TABLE I
HYDROGENOLYSIS OE OVOLECITHIN WITH LITHIUM ALUMINUM HYDRIDE

Expt. No.	I	II	III
Reaction time (min.)	10	30	60
Temperature (°C)	14	16	16
Mole ratio of L.: $LiAlH_4$	1:2	1:2	1:2
Total choline, calcd.	19.1	17.8	17.8
Total choline[8] in aq. phase	18.0	19.1	19.6
Free choline[9] in aq. phase	0.8	4.1	4.1

L. stands for lecithin.

The reaction was carried out in anhydrous ether. No significant amount of organic phosphorus was found in the ether phase nor inorganic phosphorus in the aqueous phase.

1) C. Long and M. F. Maguire, *Biochem. J.*, **57**, 223 (1954).
2) E. Baer and J. Maurukas, *J. Biol. Chem.*, **212**, 39 (1955).
3) N. G. Gaylord, *Experientia*, **X**, 356 (1954).
4) N. L. Paddock, *Nature*, **167**, 1070 (1951).
5) P. Karrer and E. Jucker, *Helv. Chim. Acta*, **35**, 1586 (1952).
6) D. N. Rhodes and C. H. Lea, *Biochem. J.*, **65**, 526 (1957).
7) D. J. Hanahan, M. S. Turner and M. E. Jayko, ibid., **192**, 623 (1951).
8) D. Glick, *J. Biol. Chem.*, **156**, 643 (1944).
9) G. Schmidt, L. Hecht, P. Fallot, L. Greenbaum and S. J. Thannhauser, ibid., **197**, 601 (1952).

As shown in Table I, glycerophosphorylcholine appears to be formed in 95% yield, accompanied by an insignificant amount of free choline under the conditions of Expt. I. The "free choline" designated in the table, however, should be questioned according to the mechanism discussed above which should give rise to trimethylethylamine. Thus, its structure remains to be investigated.

The product was isolated according to the procedure described by Baer and Kates[10], after passing the aqueous solution through a column of a mixture of IRC—50 and Dowex-3. Since only a limited amount of the product was available, a concentrated solution of the aqueous phase was used for the following determinations: P: choline, 1.0:1.02; absorption of a periodate solution, 97% of theory; and $(\alpha)_D^{24}$ -2.96 ± 0.2(in water), $(\alpha)_D^{28}$ -2.85 ± 0.1[10]. On drying the crystalline cadmium complex of the product, two moles of water was found to be lost.

Anal. Found(amorphous): P, 5.24. Calcd. for $(C_8H_{22}O_7NP)_2(CdCl_2)_3$: P, 5.62.
Found (crystalline): C, 19.66; H, 5.32. Calcd. for $(C_8H_{22}O_7NP)\cdot CdCl_2\cdot 2H_2O$: C, 19.46; H, 5.30.
Found (dehydrated crystals): C, 21.56; H, 4.80. Calcd. for $C_8H_{22}O_7NP\cdot CdCl_2$: C, 20.97; H, 4.84.

These results show that the glycerophosphorylcholine isolated has the L, α-configuration. It also suggests that the method can be utilized in obtaining L, α-glycerophosphoric acid from phosphatidic acids, and this is now under investigation.

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10) E. Baer and M. Kates, *J. Am. Chem. Soc.*, **70**, 1394 (1948).

On the State of Formic Acid Adsorbed on Dehydrated Silica

By Kozo Hirota, Kenji Fueki, Yasuo Nakai and Kotaro Shindo

(Received July 21, 1958)

It has been found recently by the kinetic method[1] and by the infrared absorption method[2] in our laboratory that formic acid is chemisorbed as the ion on some metallic powders. However, from the fact that activity of metal as an adsorbent differs from that of silica[3] it is inferred that the acid may be adsorbed on the latter in a different state. To settle the problem some physico-chemical studies were undertaken. A combined method of infrared absorption and proton magnetic resonance was adopted and some conclusions on the chemisorbed state were obtained.

Sample. — The formic acid used in the experiment was dehydrated with anhydrous copper sulfate after repeated distillations. The amorphous silica adsorbent was prepared by dehydrating commercial silica gel at 300°C over a week, and it was confirmed by X-ray analysis that the amorphous structure of silica did not change before and after the dehydration. The specific surface area of silica gel was found to be 520 m^2/g. by the BET method (adsorbate: nitrogen) and formic acid was adsorbed on silica by an amount less than that necessary to form a monolayer*.

Measurement. — The infrared spectra were obtained with the same spectrometer as used in the previous report (Hilger H 800)[2], and a paste method, in which mulling was done with Nujol, was adopted in the present research. The proton resonance spectra were obtained with a high resolution spectrometer (Varian V-4310 C) at a fixed frequency of 40 Mc/sec. Both measurements were made at room temperature.

Results and Discussion.—The infrared spectrum of formic acid adsorbed on silica is quite different from those of formic acid adsorbed on metallic adsorbents which are supported on silica, From the present results shown in Fig. 1, three conclusions may be derived. First, a broad band appears at 3537 cm^{-1}, ranging

1) K. Hirota and T. Otaki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), in Press.
2) K. Hirota, K. Kuwata and Y. Nakai, This Bulletin, in press (1958).
3) G. M. Schwab et al., *J. Am. Chem. Soc.*, **71**, 1806 (1949).
* The cross section of the formic acid molecule was assumed to be 17 A^2.

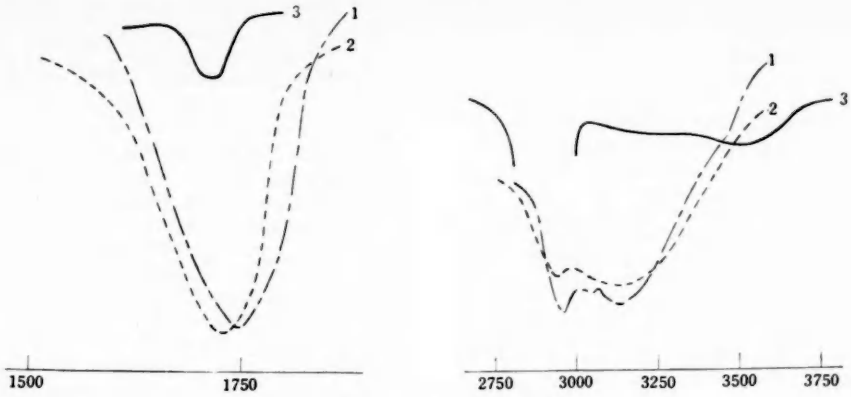
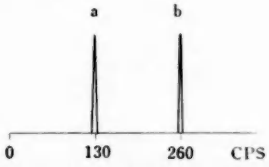


Fig. 1. Infrared spectrum of formic acid in various states.
1: vapour, 2: liquid, 3: adsorbed on silica.

from 3010 to 3765 cm^{-1}*. Such a band did not appear in the cases of formic acid adsorbed on metallic adsorbents and formic acid in the liquid state. According to Bonner and Hofstadter[4] and Wilmshurst[5], associated dimer of formic acid has a broad band near 3080 cm^{-1} which is ascribed to the formation of hydrogen bond, while monomeric formic acid has a sharp band near 3570 cm^{-1}. The band obtained in the present experiment is more similar in frequency to that of monomer than that of associated dimer, but it is broader, probably owing to the interaction between formic acid and silica.

Secondly, the antisymmetric band (ν_4) near 1580 cm^{-1}, which could be assigned to the formate ion $HCOO^-$ in the previous paper[2], is not observed in the present research. This result conforms the above suggestion that formic acid does not dissociate on the silica surface, but exists as a monomeric state. Thirdly, it is found that the C=O stretching band, whose center is at 1717 cm^{-1}, exists in lower frequency than that of monomeric formic acid[5].

The above conclusions can also be given by the proton magnetic resonance method, when the spectrum of the adsorbed formic acid is compared with that of liquid. As shown in Fig. 2, the proton resonance spectrum of liquid formic acid gives two proton signals in a lower field relative to that of water. The shift of one signal is



← Magnetic field H increasing

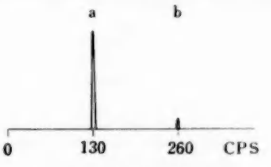
a: ^1H bonded to C. Zero of reference: H_2O
b: ^1H bonded to O.

Fig. 2. Proton resonance spectrum of formic acid.

130 cps, while that of the other is 260 cps, both intensities being the same, as is expected from the structure of the formic acid molecule.

It may be assigned from the studies on similar compounds that the former is due to the hydrogen atom bonded to the carbon atom, while the latter to the hydrogen atom bonded to the oxygen atom. To make sure of it, the proton resonance spectrum of deuteroformic acid HCOOD (90% in mol.) was measured. As shown in Fig. 3, the latter signal diminished to one tenth of the former in intensity.

However, the proton resonance spectrum of formic acid adsorbed on silica (Fig. 4)



← H increasing

Fig. 3. Proton resonance spectrum of deuteroformic acid HCOOD (90% in mole).

* This band is obtained by subtracting absorption intensity of silica alone from that of the system of formic acid-silica.

4) L. G. Bonner and R. Hofstadter, *J. Chem. Phys.*, **6**, 531 (1938).

5) J. K. Wilmshurst, ibid., **25**, 478 (1956).

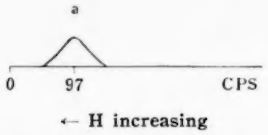


Fig. 4. Proton resonance spectrum of formic acid adsorbed on silica.

is quite different from that in liquid state; i. e., only one signal corresponding to the hydrogen atom bonded to the carbon atom appears as a broad one, its position, moreover, shifting by 33 cps to a higher field. Thus it can be concluded that the motion of hydrogen in the carboxyl group is fixed by adsorption, i. e., its free motion is hindered markedly*. Such a conclusion is in accord with the result that the OH stretching band found in the infrared spectrum becomes broad and shifts to higher frequency. It is supposed that the hydrogen bonds formed in associated formic acid decrease in number as a result of dissociation, caused by the strong adsorption of hydrogen atoms on the silica surface.

It can also be said, from the shift of the signal observed in the proton resonance spectrum of formic acid adsorbed on silica, that the electron density of the hydrogen atom bonded to the carbon atom is increased by adsorption. Detailed discussion on this result will be published later.

The authors express their sincere thanks to Professor Junkichi Itoh and Mr. Shiro Sato who measured the proton resonance spectra, and also to Mr. Tadaaki Otaki who gave them the sample of formic acid.

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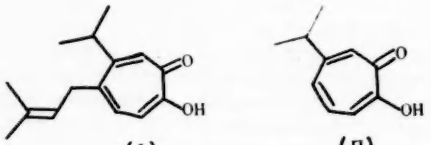
* Recently the proton resonance spectrum of acetic acid, propionic acid etc. adsorbed on amorphous silica was reported (The 11th Annual Meeting of the Chemical Society of Japan, April 6, 1958) by M. Shimizu, T. Ikegami and I. Higuchi. Their conclusion on the adsorbed state is similar to the present one.

The Synthesis of Nootkatin, a Sesquiterpenoid Tropolone[1]

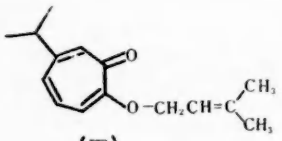
By Yoshio KITAHARA and Makoto FUNAMIZU

(Received July 31, 1958)

Nootkatin, the only known sesquiterpenoid tropolone, was isolated by Erdtman and his collaborators from the heart-wood of *Chamaecyparis nootkatensis* (Alaskan yellow ceder)[2]. The structure has been demonstrated as 4-isopropyl-5-(γ-methyl but-β-enyl) tropolone (I) by chemical reaction[2] and X-ray analysis[3]. As far as the authors are aware, the synthesis of nootkatin has not been attained as yet. This paper deals with the synthesis of nootkatin by a simple method.



(I) (II)



(III)

4-Isopropyltropolone (II) has been chosen as a starting material since (II) was synthesized before[4]. The procedure initiated from 5-substituted 4-isopropyltropolones, i. e. 5-cyano and 5-formyl derivatives derived from 5-amino-4-isopropyltropolone, was fruitless.

The Claisen rearrangement reaction has been applied to the synthesis of I. Preliminary work on the rearrangements of tropolone allyl ether and 3,7-dibromotropolone allyl ether resulted in the formation of 3-allyltropolone (80% yield) and in recovery of a small amount of 3,7-dibromotropolone, respectively, and no *p*(5)-rearrangement product was observed.

1) Presented at the 11th Annual Meeting of the Chemical Society of Japan in Tokyo, April 3, 1958. This investigation was supported in part by a donation of the Sankyo Co., Tokyo.

2) B. Carlsson, H. Erdtman, A. Frank and W. E. Harvey, *Acta Chem. Scand.*, **6**, 690 (1952); H. Erdtman and W. E. Harvey, *Chem. and Ind.*, **1952**, 1267; S. R. Duff and H. Erdtman, ibid., **1954**, 432.

3) R. B. Campbell and J. M. Robertson, ibid., **1952**, 1266.

4) T. Nozoe et al., *Proc. Japan Acad.*, **26**, No. 7, 43 (1950).

However, it seemed to us that a steric effect of dimethyl group in the cyclic intermediate of rearrangement of 4-isopropyltropolone γ: γ-dimethylallyl ether (III) might bring about a possibility of *p*-rearrangement to give nootkatin.

The reaction of silver salt[5] of II with γ: γ-dimethylallyl bromide in anhydrous ether gave an oily mixture of III and its isomer. On refluxing the mixture in xylene for three hours and treating the resulting reaction mixture with aqueous sodium bicarbonate-, sodium carbonate- and then with sodium hydroxide solution, nootkatin, m. p. 95° was obtained in 7% yield from a soluble part in aqueous sodium hydroxide solution.

Anal. Found; C, 77.61; H, 8.36. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

The identity with an authentic specimen of natural nootkatin was established by mixed melting point determination, infrared and nuclear magnetic resonance spectral comparisons.

The authors express their thanks to Professor T. Nozoe and to Professor T. Toriumi for their interest and encouragement, to Professor J. D. Roberts of the California Institute of Technology, U. S. A., for a supply of isoprene as a starting material and to Professor H. Erdtman of the Royal Institute of Technology, Sweden for a gift of natural nootkatin.

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5) H. Iinuma, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **64**, 742 (1943).

Determination of Aluminum in True Solution in the Presence of Colloidal Hydrated Alumina

By Katsumi Goto, Hiroshi Ochi and Takeshi Okura

(Received August 4, 1958)

For lack of a cenvenient method of determining small amounts of aluminum, few attempts have been made to differentiate between the aluminum in true solution and that in the colloidal form (or better, large hydroxoaquoaluminum ions[1]), except Tanaka's work[2], who separated ionic aluminum from waters containing colloidal hydrated alumina, using an ion-exchange technique.

On the other hand, a simple and accurate method, involving a chloroform extraction of aluminum as 8-hydroxyquinolate and subsequent determination of the absorbance of the extract, was recently developed by Gentry and Sherrington[3] and also by other workers.[4,5] This method was later modified by Motojima[6] to be used for the simultaneous determination of iron and aluminum, and by Goto[7,8] to prevent iron from being extracted.

It has been reported by Motojima[6] that while the extraction of aluminum 8-hydroxyquinolate is complete at pH 4.5 to 9.5, the recovery of aluminum is low when the pH of the sample is adjusted prior to the addition of 8-hydroxyquinoline. This statement seems to indicate the applicability of the above extraction method to the differentiation between the two forms of aluminum in water.

The extraction method was somewhat modified in the present investigation and actually applied to the determination of aluminum in true solution.

Method. *Reagents.—8-Hydroxyquinoline (oxine) solution.*—Dissolve 2 g. of pure 8-hydroxyquinoline in 5 ml. of glacial acetic acid and dilute to 200 ml. with distilled water. *Sodium acetate solution,* 1 M. *Chloroform. Sodium sulfate, anhydrous.*—Purest grade of commercial product often contains substances which produce a considerable blank color. Purify by recrystallization from water.

Procedure.—Take approximately 10 ml. of distilled water in a separatory funnel. Add to this 2 ml. of 8-hydroxyquinoline solution and 2 ml. of sodium acetate solution, and mix well. Pour slowly from a buret 10.0 ml. of chloroform into the separatory funnel. Do not shake at this step. Add, as rapidly as possible, 20 ml. of sample (containing less than 4 mg./l. of extractable aluminum) to the separatory funnel. The pH value must be within the range 4.5 to 9.5. Shake vigorously for about 10 sec., and allow the mixture to separate into two layers. Stable emulsions will be produced in the presence of colloidal form of hydrated alumina. It is important in

1) See H. Tanabe, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **74**, 253, 866 (1954); **77**, 33, 37 (1957).
2) M. Tanaka, This Bulletin, **27**, 98 (1954).
3) C. H. R. Gentry and L. G. Sherrington, *Analyst*, **71**, 432 (1946).
4) S. E. Wiberley and A. G. Bassett, *Anal. Chem.*, **21**, 609 (1949).
5) J. L. Kassner and K. A. Ozier, ibid., **23**, 1453 (1951).
6) K. Motojima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 903 (1955).
7) K. Goto, *Chem. and Ind.*, **1957**, 329.
8) T. Okura, K. Goto and H. Suzuki, *Industrial Water* (*Kogyo Yosui*) **2**, 338 (1956).

such a case that the emulsions are broken with a glass rod. Run the chloroform layer into a test tube containing a small amount of anhydrous sodium sulfate, which serves to remove droplets of water in the chloroform. Measure the absorbancy at 420 mμ.

Discussion.—In the usual procedure, 8-hydroxyquinoline, sodium acetate and chloroform are added to the sample in this order, and then the mixture is skaken to extract aluminum 8-hydroxyquinolate into the chloroform layer. The usual procedure can not be applied when the sample contains colloidal hydrated alumina of a very low degree of polymerization, since such colloidal hydrated alumina is also extracted to a considerable extent into the chloroform layer because of its rather rapid depolymerization. This interference from colloidal alumina, however, will be minimized by carrying out the extraction very rapidly. The procedure described in the present paper may meet this requirement. A 10 second's shaking is sufficient for the complete extraction of aluminum in a true solution at 20°C, as will be clear from Table I.

The form of aluminum available for the present method is not known strictly. However, it may be ionic or, if not, of a very low degree of polymerization, since a clear solution containing much unextractable aluminum can be easily obtained.

It has been shown by the above method that when an acidic solution of the aluminum ion is neutralized to a pH between 5 and 8, the concentration of extractable aluminum approaches the solubility very rapidly (Fig. 1) while the solution remains clear for more than 30 min. No other methods may be able to determine such a rapidly dercreasing concentration of aluminum in a true solution. Total aluminum can be determined after decomposing colloidal alumina by boiling with a small amount of hydrochloric acid. A larger amount of sodium acetate is required in this case to obtain a suitable extraction pH.

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TABLE I
EFFECT OF SHAKING TIME ON THE EXTRACTION OF ALUMINUM AT 20°C
(Concn. of Al^{3+}: 2.55 mg./l.)

Shaking time (sec.)	Recovery of Al (%)
5	102
10	99
20	99
30	99
60	100

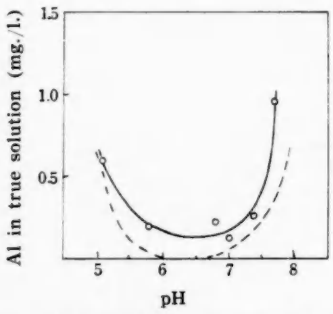

Fig. 1. Very rapid disappearance of Al^{3+} at various pH values. (25.0°; pH adjusted with NaOH)

-o-o- Al in true solution 1 min. after neutralization.
----- Solubility (see Ref. 8)
Initial concentration of Al^{3+}: 2.42 mg/l

Synthesis and Use of L-Histidine Benzylester

By Shiro Akabori, Shumpei Sakakibara and Sumiko Shiina

(Received August 5, 1958)

Up to the present, histidine methylester[1] has been known to be an only actual example of the histidine esters. Izumiya[2] attempted the synthesis of histidine benzylester, but the benzylester in a pure form was not obtained by his procedure.

In this communication, crystalline histidine benzylester di-*p*-toluene sulfonate(I) was prepared in a good yield. A suspension of powdered L-histidine hydrochloride monohydrate (20 g.), *p*-toluene sulfonic acid monohydrate(44 g.) and benzyl alcohol (100 ml.) in chloroform (500 ml.) was refluxed for about 30 hr. in Wieland's[3] apparatus, in which silica gel and anhydrous sodium carbonate were used as desiccants. Distillation of chloroform, followed by addition of dry ether (350 ml.),

1) E. Fischer und L. H. Cone, *Ann.*, **363**, 107 (1908).
2) N. Izumiya and K. Makisumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*). **78**, 662 (1957).
3) T. Wieland, G. Ohnacker und W. Ziegler, *Ber.*, **90**, 194 (1957).

TABLE I

PEPTIDE-DERIVATIVES SYNTHESIZED FROM HISTIDINE BENZYLESTER

Substance	Solubility in dil. HCl	Yield (%)	Melting point (°C)	$[\alpha]_D^{30}$	Anal. (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Cbzo-Gly-L-His-OBz[a]	+	77.9	99~100.2	−6.8°[g]	63.29	5.54	12.84	63.01	5.73	12.43
〃 [b]		82.5	98.5~99.2	−5.5°[g]						
〃 [c]		45.8	99~99.5	−6.3°[g]						
Cbzo-L-Thr-L-His-OBz[b]	+++	66.5	137~137.5	−16.4°[h]	62.48	5.87	11.66	62.48	6.19	11.80
Cbzo-L-Phe-L-His-OBz[a]	−	68.5	118~118.5	−17.3°[h]	68.42	5.74	10.64	68.44	5.95	10.76
〃 [b]		53.3	117~118.5	−22.4°[h]						
Isovaleryl-L-His-OBz[d]	+	7.6	144	−23.6°[h]	65.63	7.04	12.76	65.79	7.29	12.72
H-Gly-L-His-OH HCl[e]		80.0	174~175 (dec.)[f]	+28.5°[i]						

(a), Mixed anhydride method (isovaleryl); (b), dicyclohexylcarbodiimide method; (c), azide method; (d), this substance was obtained as a byproduct from the dil. HCl extract of the reaction mixture of Cbzo-Phe-His-OBz (mixed anhydride method); (e), dried at 135° in vacuo; (f), corrected value; M. Hunt[5] reported m. p. 175° (corr.); (g), c 2, ethanol; (h), c 1, ethanol; (i), c 1, water; M. Hunt[5] reported $[\alpha]_D^{26}$ +25° (c 1, water).

Cbzo..... Carbobenzoxy, Bz..... benzyl.

gave a syrupy mass which was reprecipitated from chloroform and dry ether. The product was then crystallized gradually from a mixture of dry dioxane and dry acetone (1 : 2); colorless fine needles, weight 48~51 g. (85~90%), $[\alpha]_D^{30}$ −2.4° (c 4.7, water). This substance I was obtained in a hydrated state on recrystallization from a dioxane-acetone mixture containing a small amount of water. The hydrated crystals could be handled more conveniently than the anhydrous because the hydrated crystals were not so hygroscopic as the anhydrous ones. Almost all of the crystallization water, if necessary, could be dried off over phosphorous pentoxide in vacuo at 30°. These properties of the hydrated crystals, however, made difficult the quantitative determination of the crystallization water. This substance I sintered at 82~85° and decomposed at 225° after dryness in vacuo at ordinary temperature, and melted at 146~149° after dryness in vacuo at 135°.

Anal. Found (dried at 135°): C, 54.95; H, 5.48; N, 7.37. Found (hydrated crystals, dried in vacuo at 30°): C, 54.90; H, 5.46; N, 6.72. Calcd. for $C_{27}H_{31}O_8N_3S_2$: C, 54.99; H, 5.30; N, 7.13%.

Histidine methylester di-hydrochloride is hard to dissolve in usual organic solvents other than methanol or ethanol; and aqueous strong alkali or sodium methoxide is required for preparing the free methylester. On the other hand, the benzylester sulfonate I was considerably soluble in dry chloroform, and a solution of I and a calculated amount of triethylamine in chloroform could be used as a free benzylester solution for peptide synthesis. For example, carbobenzoxy glycyl histidine benzylester (II) was prepared as follows. A solution of mixed anhydride, which was prepared from carbobenzoxy glycine (1.05 g.), isovaleryl chloride (0.6 g.) and triethylamine (0.7 ml.) according to Vaughan and Osato's procedure[4], was allowed to react overnight with a mixture of I (3.54 g.) and triethylamine (1.70 ml.) in chloroform (15 ml.), and after usual treatment of the reaction mixture, the substance II was obtained in a yield of 1.7 g. The substance II was then hydrogenated in the presence of Palladium charcoal into glycyl histidine hydrochloride, and it was confirmed that the product obtained here was superior in specific optical rotation to the reported one[5] which was prepared from carbobenzoxy glycyl histidine methylester. The peptide-derivatives synthesized from the histidine benzylester are listed in Table I.

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4) J. R. Vaughan Jr., and R. L. Osato, *J. Am. Chem. Soc.*, **73**, 5553 (1951).
5) M. Hunt and V. du Vigneaud, *J. Biol. Chem.*, **127**, 46 (1939).

*Proton Resonance in Sulfamic Acid**

By Shizuo FUJIWARA and Ichiro YAMAGUCHI**

(Received August 5, 1958)

Structural investigations on sulfamic acid by X-ray diffraction[1] and infrared absorption[2] measurements have shown the results to suggest the zwitter-ion form of $NH_3^+SO_3^-$ in crystal. Since nuclear magnetic resonance method is very straight-forward to distinguish two-proton system[3] from three-proton one[4], we have applied this method to the crystal of sulfamic acid. Evidences of zwitter-ion form will be shown here as well as the informations on the intramolecular rotation as the results of the measurements of line shape and widths.

Experimental.—The sample studied is crystalline powder with a purity of 99.95%. The proton resonance is observed at about 20 megacycles. The temperature range of the experiment is between −180°C and +60°C. The apparatus used is of the autodyne-detector type which has been described elsewhere[5]. Though efforts to make measurements below the temperature of liquid nitrogen were made, reliable record was not obtained as the sample was saturated.

The resonance curve has a shoulder over all the temperature range of the experiment and, furthermore, the second shoulder appears below −170°C outside of the first shoulder. Fig. 1 presents the half of the derivative of the resonance curves at several temperature ranges. With decreasing temperature, the line shape becomes of three-peaked form, the evidence of three-proton system[4]. This suggests that the zwitter-ion form can be taken plausible as the molecular configuration at this temperature range.

Fig. 2 shows the temperature dependence of the second moment of the resonance absorption curve. A constant value of about 6±0.5 gauss[2] is taken throughout the temperature range of the experiment higher than −170°C. It begins to increase in the range below −170°C, taking a value of about 12 gauss[2] at −180°C. This change in the second moments will suggest that the molecule begins to freeze at this temperature range.

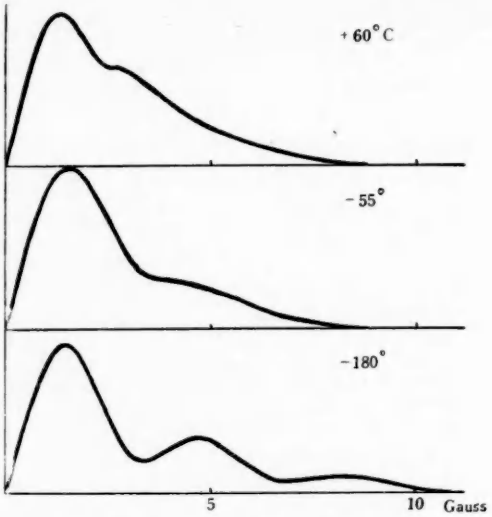

Fig. 1. Derivative of the proton resonance absorption curves for sulfamic acid at various temperatures.

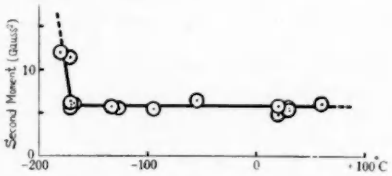

Fig. 2. Temperature dependence of the second moment.

Discussion of the Results. — Second moments are calculated for various models of the molecular structure: a) 30.7 gauss[2] for the model suggested by X-ray diffraction[1] where three protons in NH_3 group are taken equivalent, and b) 15∼20 gauss[2] for the model of NH_2SO_3H having the same structure as a) with respect to the skeleton of heavy atoms. When NH_3 group in the model a) rotates freely about N-S bond axis, the second moment is expected to be reduced to 7.5 gauss[2].

According to the results shown above, we assume that the molecule takes zwitter-ion structure in crystal and reorientates about N-S bond axis in the temperature range higher than −170°C. Sano[6] reported a value of the second moment at room temperature almost the same as that obtained by the present authors. He

* Presented at the Autumnal Meeting of the Chemical Society of Japan, held in Tokyo, November, 1957.

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explained this value by taking a model where molecules were rigid with the zwitter-ion form and N-H bonds in NH_3 groups were unusually elongated. This seems unplausible, however, since such an unreasonably deformed structure will show temperature dependence in the second moment values and, moreover, such a model can not explain the increasing tendency at around $-180°C$.

Another comment will be added here with respect to the zwitter-ion structure: asymmetrical derivative curve was obtained when the sample was moist. We assume that this curve is superposition of a narrow line and a broad one being different in resonance center. Since the intensity of the central narrow line is humidity dependent, it is attributed to the water molecules adsorbed by the sample. The asymmetrical curve was decomposed to show that the resonance center for the adsorbed water was shifted to the field higher than that for the broad line by 10^{-5}; in another words, proton in sulfamic acid is electronically less shielded than in water molecules. The asymmetrical figure of the derivative curve is not due to the saturation effect since the same result has been obtained when the polarity of the bias field is reversed.

A similar result of large positive shift has been reported with formamide[7], which is also considered to form zwitter-ion, and, therefore, the finding presented here may be taken as the characteristic nature of protons forming zwitter-ions.

Authors' thanks are due to Mr. K. Nukada of Government Chemical Industrial Research Institute and to Dr. M. Kobayashi of Tokyo University who supplied the samples for the experiments. They are also indebted to Dr. T. Sugawara of Tohoku University who made the measurements at liquid hydrogen temperature.

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Particle Size Dependence of Heat of Transition of Crystalline Trimethylamine Sulfurtrioxide, $(CH_3)_3N \cdot SO_3$

By Hiroshi Suga*, Kunio Nakatsuka** and Syûzô Seki

(Received August 9, 1958)

The crystal structure of trimethylamine sulfurtrioxide at room temperature (hexagonal) has been determined by Shimizu and MacLachlan[1] who revealed the presence of rotational disorder of $(CH_3)_3N$ and SO_3 groups about the N-S axis. This result implies that a kind of order-disorder phase transition due to disappearance of such a disordered state will take place when the crystal is cooled.

The present material was prepard by a new method by adding chlorosulfonic acid (SO_3ClH) to a chloroform solution of trimethylamine. The sample thus obtained was identified by the m. p. determination and by Norelco X-ray diffractometer. The specimens used for the measurements were recrystallized from aqueous solution and then ground to about 0.1~0.01 mm in diameter; m. p. 241~243°C (decomp.).

As we expected, the differential thermal analysis has really confirmed that the crystal undergoes a phase transition at about $-30°C$ in the cooling and at about $+20°C$ in the heating directions, showing an anomalously marked hysteresis phenomenon. Quite unusually, however, the magnitude of heat effect associated with the phase transition changes from specimen ot specimen to a considerable extent depending on their particle sizes.

To examine this effect quantitatively, the heat capacities were measured with the following specimens; specimen A, the mean particle diameter of 0.0075~0.03 mm, specimen B 0.11~0.15 mm and specimen C 0.25~0.36 mm. In the C_p-T curves of these specimens measured immediately after cooling there appears always a broad maximum (about $+17°C$) followed by irregular heat evolution and absorption (see Fig. 1). This irregular thermal anomaly, however, disappeared when the

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1) H. Shimizu and Dan MacLachlan, *J. Am. Chem. Soc.*, **75**, 4352 (1953).

TABLE I

PARTICLE SIZE DEPENDENCE OF THE HEAT OF TRANSITION

Specimen	Mean diameter (in mm)	Method of preparation*	$T_{tr.}$ (°C)	ΔH (cal./mole)	ΔS (e. u.)
A	0.0075~0.03	sublimation	+18 (heating) −38 (cooling)	80	—
B	0.11~0.15	grinding, separated by sieve set	+16 (heating) −30 (cooling)	230 230	0.80 0.98
C	0.25~0.36	〃	+16 (heating) −28 (cooling)	300	—

* The identification of the crystalline modification of the samples prepared by different methods was made by their m. p. and the Norelco X-ray diffraction patterns.

specimens were cooled down very slowly to −80°C with taking several days (see Fig. 2). After this treatment of each specimen, we carried out the measurement. It was found that the greater the particle size, the greater difficulty was encountered for obtaining the equilibrium curve.

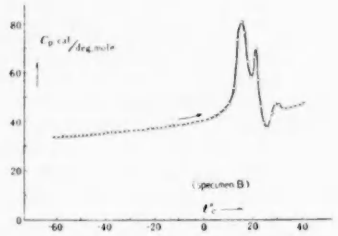

Fig. 1. Heat capacity vs. temperature curve of $(CH_3)_3N \cdot SO_3$ before the treatment.

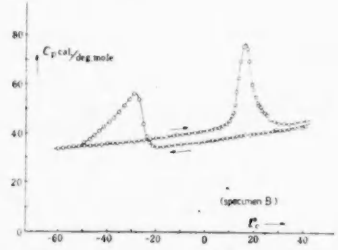

Fig. 2. Heat capacity vs. temperature curve of $(CH_3)_3N \cdot SO_3$ after the treatment.

Table I lists enthalpy changes at transition point of three different specimens. Although an effort was made to obtain true equilibrium (heating rate : 1 deg./6 min.), the values reported here are of approximate nature owing to the unusually sluggish velocity of this phase transition. Such a remarkable dependence of the enthalpy of the transition on particle size has never been reported as far as we are aware of. It is supposed that the observed heat of transition arises from at least two origins; one is the enthalpy difference between the bulk enthalpies of the two phases and the other the difference in enthalpies which come from the formation of micro-structure, such as a domain structure or submicro-region[2], on passing through the transition point.

We are now investigating the above-mentioned phenomenon by use of dilatometry, X-ray and other available methods. The detailed discussion on the present results will be reported elsewhere.

The authors wish to express their sincere thanks to Professor I. Nitta for his continued interest in the present study.

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The Structure of Stipitatonic Acid, a Mould Metabolite from Penicillium[1]

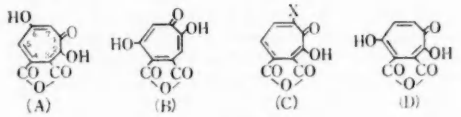
By Kôzo Doi and Yoshio Kitahara

(Received August 9, 1958)

Stipitatonic acid, a mould tropolone, $C_9H_4O_6$, m. p. 237~237.5° (decomp.) has been isolated from *Penicillium Stipitatum*

1) The paper was presented before the Local Meeting of the Chemical Society of Japan in Yonezawa, June 23, 1958. This work was supported in part by a donation of the Sankyo Co., Tokyo.

Thom. by Segal and the structure A has been assigned to it rather than the alternative isomer B[2]. We now wish to show evidence which permits the assignment of structure B to stipitatonic acid contrary to that proposed before[2].



6-Hydroxytropolone-3,4-dicarboxylic anhydride(A) and its two isomers concerning with hydroxyl group were synthesized by the following methods and these anhydrides were compared with stipitatonic acid.

Bromination of tropolone-3,4-dicarboxylic anhydride (C:X=H), an oxidation product of purpurogallin[3] gave 7-bromo compound (C:X=Br), m. p. 198°C[4]. It has been reported[5] that liquid phase hydrolysis of 3-bromotropolone afforded 4-hydroxytropolone, and a minute amount of 3-hydroxytropolone. Application of this reaction to the 7-bromo compound (C:X=Br) gave 7-hydroxy compound (C:X=OH) in 40% yield and a hydroxytropolone-3,4-dicarboxylic anhydride, m. p. 237°C (*not decomp.*), yellow needles, in 6% yield.

Anal. Found: C, 51.94; H, 1.86. Calcd. for $C_9H_4O_6$: C, 51.93; H, 1.94%. Ultraviolet maxima, $m\mu(\log \varepsilon)$ in methanol: 272(4.46), 345(3.90), 363 (3.92).

The latter anhydride, m. p. 237°C underwent decarboxylation to give stipitatic acid, m. p. 279 ~280°C[6] whose identity was confirmed by ultraviolet and infrared spectra,

Anal. Found: C, 52.43; H, 3.47. Calcd. for $C_8H_6O_5$: C, 52.75; H, 3.32%. Therefore the structure of the anhydride, m. p. 237°C. also has to be the structure A. Persulfate oxidation of the anhydride (C:X=H) gave 7- and 5-hydroxy compounds (C:X=OH and D).

Anal. Found: (5-hydroxy compound, m. p. 250°C): C, 51.79; H, 1.68%. The structure of the 5-hydroxy compound was supported by the decarboxylation to give 5-hydroxytropolone, m. p. 250°C (decomp.)[7].

Any hydroxy compound of the tropolone-3,4-dicarboxylic anhydride mentioned above was not identical with natural stipitatonic acid which was kindly spared by Dr. Segal. The proof to support the structure A for stipitatonic acid rather than the structure B has been based on the submission to azo-coupling but no detail on the azo compound is mentioned[2]. It seems to us that unless a true azo-coupling compound is produced, the test for the vacant *p*-position can be misleading because even *p*-substituted tropolones show red coloration with aryl diazonium salts.

The difference, $\Delta\nu$ between two carbonyl frequencies of anhydride group of almost all derivatives of tropolone-3,4-dicarboxylic anhydride in infrared spectra in 60 ± 2 cm^{-1}, while $\Delta\nu$ of stipitatonic acid is 78 cm^{-1} [2].

Therefore the above results and evidence that decarboxylation of stipitatonic acid gave stipitatic acid[2] suggest that *the structure of stipitatonic acid is not A but B.*

When this manuscript was completed, one of us (Y. K.) received a letter from Dr. Segal on August 6, in which he described that his observation on a potash fusion of stipitatonic acid was in complete agreement with our belief regarding the structure.

The authors wish to thank Professor T. Toriumi of this Institute for his encouragement and Dr. W. Segal for a supply of stipitatonic acid.

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Chemical State of Uranium-239 in Neutron-Irradiated Uranium(IV) and Uranyl(VI) Sulfate Solutions

By Nobufusa Saito and Tatsuya Sekine

(Received August 14, 1958)

Very few investigations have been devoted to study the chemical state of ^{239}U in neutron-irradiated uranium compounds. In 1939, Irvine[1] reported probable

1) J. Irvine, Jr., *Phys. Rev.*, **55**, 1105 (1939).

formation of quadrivalent ^{239}U in neutron-irradiated ammonium uranyl acetate solution and its enrichment with respect to ^{238}U in the first fraction of a hydrolytic precipitation by a factor of the order of ten. On the other hand, Aten, Beers and De Groot[2] reported that quadrivalent and sexivalent uranium isolated from U_3O_8 irradiated with slow neutrons have the same specific activity of ^{239}U. The following experiments have been carried out by the present authors to study the chemical state of ^{239}U in neutron-irradiated uranium(IV) and uranyl(VI) sulfate solutions.

TABLE I

COMPOSITION OF THE SOLUTIONS (in moles)

	U(VI)	U(IV)	SO_4^{--}*	H^+
Soln. A**	0.02	—	1.9	2.8
Soln. B	0.02	0.02	1.9	2.8
Soln. C	—	0.02	1.9	2.8

* SO_4^{2-} was supplied as sulfuric acid and sodium sulfate.

** Nitrogen gas was passed through the Soln. A.

Three kinds of target solution were made up as shown in Table I, and 100 ml. of each solution in a glass vessel was exposed for one hour to a neutron flux of $\sim 10^7/cm^2/sec$. During irradiation, the container of the solution was covered with a black paper to keep the whole system in the dark. In addition, it was cooled with ice to reduce the velocity of isotopic exchange reaction between uranium(IV) and uranium(VI)[3]. After irradiation, either uranyl(VI)- or uranium(IV) sulfate was added to the solutions A and C, so that the solutions became 0.02 M in both uranyl(VI)- and uranium(IV) sulfate. The separation of uranium(IV) from uranium(VI) was carried out with portions of the resulting solution within 30 minutes after the end of irradiation. The uranium(IV) fraction was extracted with chloroform as cupferronate. After the solvent and the excess of cupferron were removed from the chloroform layer, the residue was dissolved in nitric acid. To the resulting solution containing uranium(VI) were added ammonia water to precipitate ammonium diuranate. The precipitate was dissolved in a hot mixture of acetic and nitric acids; finally sodium uranyl acetate was precipitated from the solution. The uranium(VI) fraction in the aqueous layer after the chloroform extration was treated in a similar way as above to precipitate sodium uranyl acetate. All precipitates of sodium uranyl acetate were dried, mounted on a stainless-steel dish and submitted to counting with a thin end-window Geiger-Müller counter. The decay of the activity was followed for more than three half-lives of ^{239}U, and the distribution of ^{239}U in uranium(VI) and uranium(IV) fractions was calculated. The results are shown in Table II.

TABLE II

RADIOACTIVITY OF ^{239}U IN EACH FRACTION

	^{239}U in U(VI) fraction		^{239}U in U(IV) fraction	
	c.p.m.	%	c.p.m.	%
Soln. A	7200	97	250	3
Soln. B	9750	75	3280	25
Soln. C	4630	61	2930	39

Remarks: Decay correction was made for each fraction. If U(III) were formed, it should be air-oxidized to U(IV) state during the separation procedure and counted as U-(IV) fraction.

In another experiment with the solution C, it was found that ^{239}U is enriched in the uranium(VI) fraction by a factor of approximately 50. From those data, the following conclusions can be drawn.

i) Most part of ^{239}U in the neutron-irradiated uranyl(IV) sulfate solution is in the sexavalen state.

ii) More than half of ^{239}U in the neutron-irradiated uranium(IV) sulfate solution is not in the quadrivalent state, but in the sexavalent state.

iii) Hot-atom effect plays an important role in the formation of ^{239}U in the sexivalent state, since ^{239}U is enriched in the uranium(VI) fraction separated from the neutron-irradiated uranium(IV) sulfate solution.

The details of this work will be reported elsewhere.

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